INORGANIC CHEMISTRY

ACCORDING

TO THE PERIODIC LAW

BY

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—AND—

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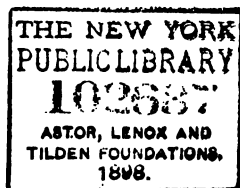
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PREFACE

So many text-books of chemistry have appeared in recent years that a new publication should be required to show just cause for its existence. The claim made in behalf of this present book is that it takes the Periodic System for its guiding principle throughout. The Periodic Law has come to be the great central fact of chemistry. It has thrown new light upon the study of the science and is the very best aid to that study. The complete introduction of this system has not been attempted in any text-book that has come to our notice. Some give brief mention of the law and then continue along the old lines as if the law were unknown ; others introduce it partially while still clinging to remnants of the old systems.

Following the advice given by Lothar Meyer in his lecture before the German Chemical Society, we have made the experiment of a complete and faithful introduction of this system and the experience of several years with our classes has convinced us of its great value. In no other way have we been able to secure such excellent results both as to thorough, systematic instruction and economy of time. The task is rendered easier for both student and teacher.

The experiments accompanying the text are those

which have been found by experience to impress the subject best upon the student. Elaborate experiments have been omitted because the time for laboratory work is usually limited and because the manipulation of such experiments tends often to distract the attention of the beginner from the principle or fact which is to be emphasized. One hour of laboratory work in connection with each lecture has been found ample time for these experiments with most college students. The experiments should be performed under the immediate supervision of an instructor and the notes kept by the student should clearly set forth what each experiment is intended to illustrate.

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PART I

INTRODUCTION

1. Chemistry is the study of matter and the changes produced in that matter by the action of chemical force upon it.

2. Matter is that which occupies space. We become sensible of its existence in mass through one or more of the senses. Thus a piece of chalk, wood, iron, a volume of water, the air around us, are all forms of matter.

There are three divisions of matter : *mass*, *molecule*, and *atom*.

3. Mass is any form of matter which is appreciable to the senses. The illustrations of matter given above were all masses of matter. These masses are made up of a great number of very small particles.

4. The Molecule is the smallest particle of matter which still retains the properties of the mass. It is too small to be appreciable to the senses. There are as many different kinds of molecules as there are kinds of mass. These particles, even in apparently rigid masses, are supposed to be in incessant and rapid motion. A molecule may be further defined as the smallest particle of matter capable of independent existence.

5. The Atom is the smallest subdivision of matter. Atoms are themselves indivisible. They unite to form molecules. They are, as a rule, incapable of independent existence. There are some seventy different kinds of

and indestructible. The principle of the indestructibility of matter is another one of the foundation-stones of modern chemistry. Furthermore not one of these atoms can be created or newly made. The total number of these atoms, therefore, within the reach of man can neither be added to nor diminished. He can change only the nature and number of the molecules.

12. Weight.—All bodies are attracted toward each other with a force proportional to the amount of matter they contain; *i.e.*, their mass. Their attraction toward the earth, that is, their weight, is the measure of their mass. This is strictly true only when matter is weighed in a vacuum, or outside of the buoyant influence of the surrounding atmosphere. This is called the absolute weight. Thus a liter of air weighs in the air o gram, whereas in a vacuum its weight is 1.293 grams. This is its absolute weight. Under ordinary circumstances the weight of a substance in air is taken as the measure of its mass.

13. Specific Weight or Specific Gravity (sp. gr.) is the relative weight of a certain volume of a substance, compared with that of the same volume of some standard substance under the same conditions. For liquids and solids the standard is water. For gases it is air.

14. Physical States.—There are three states of aggregation or physical states, *solid*, *liquid*, and *gaseous*. A mass of matter must exist in one or the other of these. They differ in the relation of the molecules to one another.

In *solids* the molecules are in close proximity and the attraction between them is strong; there is but little freedom of motion between the molecules. Such a body is able to retain a definite form.

In *liquid* the molecules are still in close proximity but the attraction between them is relatively less strong

than in solids and there is much greater freedom of motion of the particles, with greater ease of change of relative position. Such bodies must be supported by the sides of some containing vessel in order to retain their form.

In *gases* the molecules are much farther removed from one another. Attraction between them is relatively very feeble and owing to the rapid motion of the molecules they are repelled from each other and only restrained within their limits of distance by pressure from without.

15. Properties of Gases.—*a. Effect of Heat.*—When a gas is heated it expands and this expansion is proportional to the absolute temperature. The absolute zero, where all motion of the molecule ceases, is—273° and the absolute temperature is obtained by adding the observed degrees centigrade to 273. We may also express the effect of heat on gases in the following manner : On heating, a gas expands $\frac{1}{273}$ of its volume at 0° for each additional degree. Zero, or the temperature at which water freezes, is usually taken as the standard temperature for the measurement of gases.

Experiment 1.—Fit a cork with a small delivery-tube in a dry test-tube. Place the test-tube in a flask partly filled with water and immerse the end of the delivery-tube in a beaker of water. Heat the water in the flask until no more air escapes from the delivery-tube. Why does it escape ? Remove the test-tube from the flask, keeping the end of the delivery-tube still under water. After the tube has cooled, estimate the volume of the air left in the tube and take its temperature, and calculate the temperature to which the tube was heated.

b. Effect of Pressure.—The volume of a gas varies inversely with the pressure. The pressure of the atmosphere at the sea-level is able to sustain a column of mercury 760 mm. high and this is taken as the standard pressure for

the measurement of gases.   Such a column of mercury
having a cross-section of one square inch, weighs nearly
fifteen pounds, or a column having a cross-section of one
square centimeter weighs one kilo.   This therefore
measures the pressure of one atmosphere.   Great pres-
sures are measured by atmospheres.

   c. Density.—The density (this term being properly
applicable to gases only) of a gas corresponds to the
specific gravity and is the relative weight of a definite vol-
ume of the gas compared with the weight of an equal vol-
ume of hydrogen measured under the same conditions
of temperature and pressure.   Hydrogen is taken as the
standard of measurement as it is the lightest gas known.
Thus, since the weight of one liter of oxygen is sixteen
times that of a liter of hydrogen, the density of oxygen
equals 16.   Similarly the density of nitrogen is 14, of
chlorin is 35.4, etc.

   In 1811 an Italian physicist, Avogadro, propounded
a theory which has proved of great use in the advance-
ment of chemistry.   This theory was designed to explain
the facts that all gases expand and contract alike under
the influence of heat and pressure, and secondly that in
combining with one another the volumes uniting bear a
simple ratio to one another and to the volumes pro-
duced.   The theory is that equal volumes of all gases
under the same conditions of temperature and pressure
contain the same number of molecules.   It follows then
that the weights of the molecules of a gas will be pro-
portional to the density of the gas.   The standard of
molecular weight (relative weight of a molecule) is taken
as one-half the weight of a molecule of hydrogen, as this
molecule is composed of two atoms.   Hence, it follows
that the molecular weight of any gas is twice the density,
or conversely, the density is one-half the molecular

weight. The density of gases may be obtained by weighing equal volumes under the same conditions.

d. Diffusion of Gases.—When gases of different densities come in contact, they do not yield to the law of specific gravity, which would separate them into strata according to their respective densities, but their molecules become uniformly distributed through the entire space. This property, which is manifest to a degree in all fluid bodies and is partly exhibited also by solids, is perfectly exhibited only in gases, and is known as diffusion. The fact of diffusion depends entirely upon the motion of the individual molecules and its rapidity on the rapidity of motion of the molecules. This motion is dependent upon the weight of the molecule and it has been shown that the rapidity of diffusion of a gas varies inversely as the square root of its density. Thus, hydrogen (density 1) diffuses four times as rapidly as oxygen (density 16). Let us suppose that a vessel containing hydrogen is placed above a vessel containing air which is more than fourteen times heavier. According to the law of gravity these two gases should retain these relative positions even though there be free exchange possible between the two vessels. The truth is that they will diffuse or mix thoroughly, and if a porous diaphragm lie between them there will be an increase of pressure in the vessel containing the air as the hydrogen passes in more rapidly than the air can come out. Thus, if a plaster jar fitted with a tube (Fig. 1), closed with a little colored water, acting as a gauge, have a jar of hydrogen placed over it, the hydrogen will rush through the sides of the jar and the water in the gauge will be

Fig. 1.

forced out. The jar B must be lowered over A and entirely surround it.

16. Changes of Physical State.—It is quite possible to change a substance from one state of aggregation, or physical state, to another. These changes in the direction from solids through liquids to gases are brought about by increasing the temperature or diminishing the pressure. The increase of temperature causes a more rapid motion of the molecules and forces them farther apart. In the reverse changes from gas through liquid to solid, the removal of heat (cold) or increase of pressure are the agencies used.

Experiment 2.—Heat a few grams of sulphur in a test-tube until the fused sulphur boils. Compare the different states of aggregation.

a. Fusion.—Where solids pass, under the influence of heat, to the liquid state, the process is known as fusion and the temperature at which the change takes place is called the fusing- or melting-point (m. p.). Some substances suffer a change of composition upon fusing. The reverse change from liquid to solid is called solidification, or, in the case of water, freezing.

b. Evaporation.—When a liquid is changed into a gas by heating or by reduction of the pressure, it is called vaporizing or evaporating it. The reverse change, brought about by cold or pressure or often both, is condensation or liquefaction.

c. Sublimation.—Some substances pass on cooling directly from the gaseous state to the solid. This is called sublimation. Such substances may, on heating, pass directly from the solid to the gaseous state.

Experiment 3.—Sublime arsenic in a closed tube (matrass). See Fig. 11, *Exp. 47.* Sublime ammonium chlorid.

d. Ebullition or Boiling.—The molecules of a liquid being always in motion (the rapidity of their motion being dependent upon the temperature), molecules at the surface of the liquid are constantly escaping from the attraction of the adjacent molecules. If the space above the liquid is confined, molecules will constantly fall back into the liquid and be held by the attraction of the molecules of the liquid. An equilibrium will soon be reached, when in a given time as many molecules will be recovered by the liquid as escape from it. The pressure of the gas above the liquid is known as the vapor-tension of the liquid for that particular temperature, and depends upon the number of molecules in a unit of space. If the temperature of the liquid be raised, the molecules will move more rapidly, more will escape, and the vapor-tension be correspondingly increased. If the space above the liquid be open, the atmosphere will normally exert a pressure upon the liquid of 760 mm. If the liquid now be heated, when the vapor-tension reaches 760 mm. the pressure of the atmosphere will be overcome and the molecules of the liquid will escape freely. The temperature for a given liquid at which this takes place is its boiling-point (b. p.). If the pressure be less than 760 mm., the liquid will boil at a lower point ; if more than 760 mm., at a higher temperature. Thus the boiling-point of a liquid would be lower upon a mountain than at the sea-level. The boiling-point is therefore dependent upon the nature of the liquid and the pressure of the atmosphere.

Experiment 4.—Heat water in a beaker or flask until it boils. Note the temperature and the barometric pressure.

17. Evaporation has already been explained as denoting the change from a liquid to a gaseous state. The term is generally applied to the escape of molecules from the

surface of a liquid at temperatures below its boiling-point. Its rapidity depends upon the vapor-tension of the liquid at the given temperature; *e. g.*, at ordinary temperatures mercury has a very low vapor-tension ; bromin a very high one. When the vapors of a liquid are cooled, the vapor-tension is reduced and the excess of vapor returns to the liquid state.

18. Distillation.—The process of boiling a liquid and condensing its vapor back to a liquid, is known as distillation, and is a process much used in chemistry for the purification of liquids. Non-volatile impurities present are not converted into vapor when the liquid is boiled and thus the liquid may be freed from them.

Direction to student.—Describe the process of distillation as carried out in the laboratory.

19. Liquefaction of Gases.—When a vapor is submitted to a pressure greater than its vapor-tension at the temperature used it will be condensed to a liquid. By means of pressure and reduction of temperature, all known gases have been condensed to liquids with the exception of hydrogen and helium. For each gas there is a temperature above which no amount of pressure will convert it into a liquid. This temperature is known as the critical temperature. Thus, the critical temperature of hydrogen is —229°, and above that no pressure can condense hydrogen to a liquid. For oxygen it is —118°, for carbon dioxid +31°, and for water +365°.

20. Solution.—A solution is an apparently homogeneous liquid mixture of two or more substances. One of the substances is usually liquid and is called the solvent. In the solvent may be dissolved gases, liquids, or solids. The solubility of a substance varies with the temperature. In general, with increased temperature, gases

become less soluble, and liquids and solids more soluble. Solution is accompanied, generally, by a contraction of volume and a change of temperature. It may or may not be accompanied by a change of composition. When a substance is dissolved in a liquid the freezing-point of the liquid is lowered while the boiling-point is raised. The amount of depression of the freezing-point or elevation of the boiling-point bears a definite relation to the molecular weight of the substance. In this way it is possible to determine the molecular weights of substances which can not be weighed in the gaseous state.

Experiment 5.—Dissolve salt in water in the proportion of about one to ten, and take the boiling-point of the solution. Compare with that of pure water.

21. Crystallization.—When a solution contains all the dissolved substance which it will hold at a certain temperature it is said to be saturated. If now the temperature be changed to a lower one at which the solvent requires less of the substance to saturate it, the excess will separate out. In the case of solids the substance very often separates out in masses bounded by regular planes and with regular angles. Such masses are known as crystals and this process is known as crystallization. A similar result may be obtained by allowing the solvent to evaporate until too little is left to hold all of the substance in solution; or by melting the substance without making use of any solvent and allowing it to cool slowly; or by heating the substance until it is changed to a vapor and allowing it to condense. In each case it is evident that it is necessary for the particles of the body to be brought into a condition in which they are free to move easily among each other, and then to give them time for the selection of their relative positions. Some bodies show no tendency to assume these regular

geometric forms and so are called *amorphous* (without form).

Experiment 6.—Dissolve as much alum in boiling water in a test-tube as the solution will take up. Cool the solution under the cold water faucet while shaking gently. Dry the crystals on filter-papers and examine with a lens.

22. Supersaturation.—A supersaturated solution is one which temporarily contains more of the substance than it is ordinarily capable of holding in solution at that temperature. It may be obtained in some cases by carefully lowering the temperature below the point at which crystallization should take place. On adding a minute crystal of the dissolved substance, or some foreign particle, or even on agitation, crystallization takes place at once.

23. Water of Crystallization.—Certain substances on assuming the crystalline state from aqueous solution appropriate to themselves a certain portion of water, the water becoming a part of the molecule and hence entering into the structure of the crystal. This water is known as *water of crystallization*. It is necessary for the formation of the crystal and often confers upon it such properties as color, etc.

24. Efflorescence and Deliquescence.—Substances which lose their water of crystallization on exposure to the air are *efflorescent* ; *e. g.*, sodium carbonate, copper sulphate. On the contrary, some solids withdraw moisture from the air, thereby becoming themselves moist or even dissolving in the water they have absorbed. Such substances are called *deliquescent* ; *e. g.*, calcium chlorid. Substances which condense small traces of moisture on their surface are often called *hygroscopic*.

Experiment 7.—Heat in a closed tube a crystal of copper sul-

phate and notice what is given off, and the change in appearance.

Experiment 8.—Repeat the experiment using alum.

Experiment 9.—Expose a fresh, clear crystal of sodium carbonate to the air for twenty-four hours, and notice any change.

Experiment 10.—Expose a piece of calcium chlorid to the air for a day or two and notice any change.

25. Latent Heat.—In every change of state of aggregation there is always either an absorption or an evolution of heat. Thus if a pound of water, which has a temperature of 0° and is just on the point of freezing, be heated by a flame capable of raising it 5° every minute, at the end of sixteen minutes the water will have reached a temperature of 80°. If a pound of ice whose temperature is also 0° be heated by the same flame for the same length of time, it will merely be melted and will still show the temperature 0°. The heat thus absorbed is the latent heat and is utilized in overcoming the cohesion of the particles and assuring them that freedom of motion which is necessary for the liquid state. If the water be turned back into solid ice, this heat is no longer required, and should be liberated. It is a well-known fact that water in freezing does give off a large amount of heat which was before latent or hidden. When a liquid is changed into a gas there is again absorption of heat and in much larger amount than was noticed in the change from solid to liquid. The reason is the same. This heat is given back or becomes sensible heat on condensing the gas into a liquid. There are many practical applications of latent heat, as in the common ice machines. In these machines the water to be frozen is surrounded by liquefied ammonia. This, on turning into ammonia vapor, absorbs sufficient heat from the water to freeze it.

Experiment 11.—Suspend a thermometer in a flask partly filled with water. Bring the water to boiling, watching the temperature. Take the temperature of the escaping steam.

LIST OF ELEMENTS WITH SYMBOLS AND ATOMIC WEIGHTS.

Name.	Symbol.	At. Wt.	Name.	Symbol.	At. Wt.
Aluminum,	Al.	27.11	Molybdenum,	Mb.	95.99
Antimony (Stibium),	Sb.	120.43	Neodymium,	Nd.	140.80
Argon,		[39.8]	Nickel,	Ni.	58.69
Arsenic,	As.	75.01	Nitrogen,	N.	14.04
Barium,	Ba.	137.43	Osmium,	Os.	190.99
Bismuth,	Bi.	208.11	*Oxygen*,	O.	16.00
Boron,	B.	10.95	Palladium,	Pd.	106.36
Bromin,	Br.	79.95	Phosphorus,	P.	31.02
Cadmium,	Cd.	111.95	Platinum,	Pt.	194.89
Calcium,	Ca.	40.07	Potassium (Kalium),	K.	39.11
Carbon,	C.	12.00	Praseodymium,	Pr.	143.60
Cerium,	Ce.	139.35	Rhodium,	Rh.	103.01
Cesium,	Cs.	132.89	Rubidium,	Rb.	85.43
Chlorin,	Cl.	35.45	Ruthenium,	Ru.	101.68
Chromium,	Cr.	52.14	Samarium,	Sm.	150.26
Cobalt,	Co.	58.99	Scandium,	Sc.	44.12
Columbium (Niobium),	Cb.	93.73	Selenium,	Se.	79.02
Copper (Cuprum),	Cu.	63.60	Silicon,	Si.	28.40
Erbium,	Er.	166.32	Silver (Argentum),	Ag.	107.92
Fluorin,	F.	19.06	Sodium (Natrium),	Na.	23.05
Gadolinium,	Gd.	156.76	Strontium,	Sr.	87.61
Gallium,	Ga.	69.91	Sulphur,	S.	32.07
Germanium,	Ge.	72.48	Tantalum,	Ta.	182.84
Glucinum (Beryllium),	Be.	9.08	Tellurium,	Te.	127.49
Gold (Aurum),	Au.	197.23	Terbium,	Tb.	160.00
Helium,	He.	[3.96]	Thallium,	Tl.	204.15
Hydrogen,	H.	1.008	Thorium,	Th.	232.63
Indium,	In.	113.85	Thulium,	Tu.	170.70
Iodin,	I.	126.85	Tin (Stannum),	Sn.	119.05
Iridium,	Ir.	193.12	Titanium,	Ti.	48.15
Iron (Ferrum),	Fe.	56.02	Tungsten (Wolfram),	W.	184.83
Lanthanum,	La.	138.64	Uranium,	U.	239.59
Lead (Plumbum),	Pb.	206.92	Vanadium,	V.	51.38
Lithium,	Li.	7.03	Ytterbium,	Yb.	173.19
Magnesium,	Mg.	24.28	Yttrium,	Yt.	89.02
Manganese,	Mn.	54.99	Zinc,	Zn.	65.41
Mercury (Hydrargyrum),	Hg.	200.00	Zirconium,	Zr.	90.40

The base of this system is $O = 16$. The atomic weights of argon and helium are very doubtful. The list is in accord with F. W. Clarke's recalculations for 1898.

26. Classifications of the Atoms.—The study of these seventy-four different kinds of atoms and their compounds would be a very serious task if there were not some mode of classifying or systematizing them. Fortunately these atoms are found to possess certain resemblances and analogies which enable us to classify them. Four different bases of classification may be considered : (1) affinity, (2) valence, (3) electrochemical character, and (4) atomic weight.

27. Affinity or Quality of Combining Power.—The attraction which exists between atoms and holds together the atoms in the molecule, is known as chemical affinity. It is a primitive, permanent and constant force, depending wholly on the nature of the unchangeable atom. This force can act only when the atoms are in close proximity (insensible distances from each other), and its strength varies with the kind of atoms united. The affinity between atoms of a widely different chemical character is much stronger than that between those of a like character, and is generally less between those of the same kind than between those of different kinds ; $e. g.$, the compound H_2O is very stable while Cl_2O is so unstable that it is easy to cause its atoms to separate. When copper and sulphur are heated together they unite. A copper atom and a sulphur atom each leaves the other atoms of the same kind, and they join so as to form a new kind of molecule in which copper is united to sulphur.

Experiment 12.—Put a few grams of copper turnings and half as much sulphur in a test-tube. Heat them in the flame until reaction takes place, as shown by the glowing of the copper. After the tube has cooled, break it and examine the contents, comparing them with the copper and sulphur used.

28. Valence or Quantity of Combining Power.—Each atom possesses a certain quantity of combining power, in virtue of which it is enabled to hold a certain number of other atoms. This bears no relation to the quality of its combining power; that is, whether its affinity is strong or weak. Thus, one chlorin atom can hold one hydrogen atom, one oxygen atom can hold two, one nitrogen atom three, and one carbon atom four. And so we might draw up the elements in series according to the number of hydrogen atoms they can combine with or, where they will not combine with hydrogen at all, with some equivalent of it. The quantity of combining power is called the valence of the atom. This is not solely an inherent property of any one atom, but is, at least partly, dependent upon the mutual influence of the atoms upon one another. The hydrogen atom is taken as the standard of the quantity of combining power, since no atom is known to possess less. An atom which combines with a single hydrogen atom or its equivalent, and thus has the same valence as hydrogen, is univalent. An atom which combines with two hydrogen atoms is bivalent. An atom which combines with three hydrogen atoms is trivalent, and with four hydrogen atoms is quadrivalent. One quadrivalent atom will combine with two bivalent atoms; three bivalent atoms will combine with two trivalent atoms, etc. A univalent atom is often spoken of as having one unit of combining power or one bond of affinity; a bivalent atom as having two units or bonds, etc. Save under a few exceptional conditions every unit of combining power is joined to some other atom. It is then said to be satisfied and the atom is saturated. It has no further power of combining with any other atom, until some one of those already held is given up. Units of combining power must not be thought of as actual

bonds or links or hooks. This is merely a figurative way of expressing the quantitative combining power of the atom. We are at a loss for a definite conception of how the atoms are held together. Valence is not fixed but is variable within certain limits. Thus, the phosphorus atom may be trivalent or quinquivalent; the sulphur atom may be bivalent, quadrivalent, or sexivalent.

29. Electrochemical Character.—The atoms may be classified by their electrochemical character. If a binary compound (one containing two elements) be decomposed by means of an electric current, one of the constituent elements will go to the positive pole and the other to the negative. The former is said to be electronegative and the latter electropositive. The intensity of the electrochemical character of the different elements varies very widely. Thus, in every combination oxygen is strongly electronegative and sodium electropositive. Sulphur while generally electronegative, as for instance towards sodium, is electropositive towards oxygen. The electrochemical character of an element then is not absolute but relative, depending upon the combination in which it is present. Furthermore, there is no unit of measure or standard by which this characteristic could be accurately determined. It is evident, therefore, that a classification of the elements by means of their electrochemical power would present many difficulties if that were the only deciding characteristic. Formerly they were divided up into metals and non-metals, these divisions corresponding in general to the more electropositive and the more electronegative elements. But the line of demarcation between these divisions could never be accurately drawn and as the old names metals and non-metals are misleading and unnecessary it would seem best to give them up.

30. Classification by the Atomic Weights. — The fourth method of classifying the atoms is by the atomic weights. Each element has its own constant atomic weight. We are therefore dealing with something fixed and capable of exact measurement, and this should give a basis for a thorough classification of the elements. Still, a classification to be true must take note of all four of the properties mentioned as affording bases for the purpose.

31. The Periodic System is a correlation of these four methods, and is based upon them all though it has been more especially worked out by a consideration of the atomic weights. In it, we have a classification which is at once strictly scientific and available as a foundation for our chemical study. This might well be called the '*natural system*.' With it are associated chiefly the names of Newlands, Mendeléeff, and Lothar Meyer.

When the elements are arranged, one after the other, in the order of their increasing atomic weights, beginning with lithium, thus:

1	2	3	4	5	6	7
Li, 7 :	Be, 9 :	B, 11 :	C, 12 :	N, 14 :	O, 16 :	F, 19

8	9	10	11	12	13	14
Na, 23 :	Mg, 24 :	Al, 27 :	Si, 28 :	P, 31 :	S, 32 :	Cl, 35.5

it is found that after the first seven the eighth element has analogous properties with the first, the ninth with the second, and so on through the seven to the fourteenth. Then in the fifteenth there is again a recurrence of analogous properties to those of the first and so to the twenty-first. These elements then might very well be arranged in sevens directly under each other.

Li 7	Be 9	B 11	C 12	N 14	O 16	F 19
Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5
K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55

32. Statement of the Law.—The statement of the Periodic Law is, that when the elements are arranged in an ascending series according to their atomic weights they fall into periods of seven and in every eighth element there is a recurrence of the properties of the first, etc. This would then enable us to arrange all the elements in seven groups or columns of analogous elements. It is noticed, however, that after the first two periods of seven the remaining pairs of sevens, are separated by short periods of three where the atomic weights are very close together. Thus, we have the third period beginning with potassium and ending with manganese; then there is a period of three, iron, cobalt, and nickel, and then the period of seven from copper to bromin. These short periods necessitate an eighth column. The latter part of the table is not completely filled out. Some elements at present known, but too imperfectly to include in the table, may fall in these places. Others may yet be discovered.

33. Reasons for Accepting the Table.—The chief reasons for accepting the table are (1) the manifest natural law underlying it and its simplicity; (2) the corrections which it has brought about in the previously accepted atomic weights and properties of certain elements; and (3) the fact that several elements have been predicted by means of the table, and have been discovered, with properties agreeing with those predicted for them. In the present state of the science of chemistry, any table is necessarily imperfect and incomplete. This table therefore presents some difficulties which, however, need not prevent its full acceptance for our present purposes. The subjoined table, which will be used as the basis of our study, is a modification of that of Mendeléeff.

THE PERIODIC SYSTEM.

GROUP.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Characteristic Valence to Hydrogen.				MH_4	MH_3	MH_2	MH	
Characteristic Valence to Oxygen.	M_2O	MO	M_2O_2	MO_2	M_2O_5	MO_3	M_2O_7	MO_4 to MO
Group Element.	Li	Gl	B	C	N	O	F	?
Type Element.	[H] Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35	
	K —	Ca —	Sc —	Ti 48	V —	Cr —	Mn —	Fe 56 ...... Co 59 ...... Ni 58
	Cu 63	Zn 65	Ga —	Ge —	As 75	Se —	Br —	
	Rb —	Sr —	Y —	Zr 90	Cb —	Mo 92	—	Ru 104 Rh 103 Pd 106
	Ag 108	Cd 112	In 114	Sn 118	Sb 120	Te 127	I 127	
	Cs 133	Ba 137	La 138	Ce 140	Ta 183	W 184	—	Os 191 Ir 193 Pt 195
	Au 197	Hg 200	Tl 204	Pb 207	Bi 208	U 239		
				Th 232				

SERIES. + − + − + − + − + − + −

34. Arrangement by Valence.—On examining the table it will be seen in the first place that it makes an easy and orderly presentation of valence. The valence of the elements increases regularly from the first column to the seventh when measured with oxygen. All elements in the first column are univalent, those in the third trivalent, fifth quinquivalent, seventh septivalent, etc. This is indicated as M_2O, M_2O_2 or MO, M_2O_3, etc. Measured by hydrogen the valence is one for both the first and seventh columns and then increases regularly from both extremes to the central or fourth column where it is four. As hydrogen does not readily combine with the first three groups the valence toward hydrogen is not indicated, but for the remainder it is represented as MH_4, MH_3, MH_2, MH.

35. Arrangement by Affinity.—The table also reveals the strength of affinity as far as this force, so difficult to measure, can be estimated. Thus, in each group the most energetic and active elements are among the first or those of low atomic weight.

36. Electrochemical Arrangement.—Lastly, as to the electrochemical character, the electropositive elements fall in the columns to the left of the fourth column and the negative elements in the columns to the right. The most intensely electronegative and positive elements are in the extreme groups and this character loses in intensity until in the central or fourth group some are positive and some are negative. As a rule throughout the groups the electronegative character diminishes with the increase in atomic weight. Since this is a relative property an element will be more negative than an element in a group to its left, and more positive than one in a group to the right.

37. Explanation of Table.—The first period of seven contains the group elements. These are also known as the bridge elements since they show many cross analogies to the elements of the immediately neighboring groups and serve to bridge over from one group to the other. The second period gives us the typical or type-elements. These give, in most pronounced form, the characteristic properties of the group. Following upon this type-element are two series usually of three elements each, which from their relative positions of right and left are called the negative and positive series. In a positive group the positive series shows a closer relationship to the type, though both series will show many analogies. In the negative groups the negative series are more like the type. While it is difficult to grasp all of the details by this brief preliminary study of the table, its continued use will tend to fix them and to reveal many of the inter-relations of these elements which can be brought out in no other way.

38. Nomenclature.—The modern systematic chemical nomenclature was introduced in part by Lavoisier, towards the close of the last century as a substitute for the phlo-gistic nomenclature then in use, the theory of phlogiston having been overthrown by him. This has been developed and improved with the increase of knowledge and the process of change is still going on. Many of the old names used by the alchemists have been dropped and are forgotten, though some traces of them are still to be found as "lunar caustic," "sal ammoniac," "oil of vitriol," "aqua regia," etc.

39. Names of Elements.—The elements are often named from some characteristic property, as bromin from $\beta\rho\tilde{\omega}\mu os$ a stench ; from some prominent compound of the element

as nitrogen (generator of nitre); after one of the planets
as uranium; or after the native land of the discoverer
as germanium, gallium. The termination *ium* (*um*), was
generally given to those elements which were regarded
as metals. This must not be taken as a guide to the
character of the element however.

40. Names of Compounds.—In compounds containing
two elements (binary compounds), the full name of the
more positive element is given followed by the more nega-
tive with its last or last two syllables changed to *-id*; *e.g.*,
sodium chlorid, NaCl; potassium bromid, KBr; mag-
nesium oxid, MgO; zinc sulphid, ZnS; etc. If two
elements form more than one compound with each other,
the more negative element may have a prefix as *di-*, *tri-*,
or the termination of the more positive may be changed to
-ic or *-ous*, *-ic* denoting relatively more of the negative
element, *-ous* relatively more of the positive. Thus,
$FeCl_2$ is iron dichlorid or ferrous chlorid; $FeCl_3$ is iron
trichlorid or ferric chlorid. These examples suffice to
give some idea of the system. It will be easier to learn
it as it is developed during the study of the compounds
themselves.

Direction to the Student.—It is a good practice for the student
to make a list of the laboratory reagents, writing out the for-
mula and the full name of each.

41. Reactions.—The expression 'chemical reaction',
broadly used, refers to any chemical change; that is,
any change in the composition of the molecule. It is,
however, especially used when it is the intention to study
the nature of the change and of the substance decomposed
or formed. The term reagent is used of the substance
which is added to bring about the change. Every
chemical reaction may (if we know what takes place)
be represented by an equation. Every chemical equa-

tion shows what takes place in sample molecules and hence represents what takes place in the whole mass. It seldom happens, however, that any one chemical reaction takes place unaccompanied by other reactions. Several different changes may be taking place in neighboring molecules of the mass at practically the same time.

42. Chemical Equations.—Our chemical equations often represent only the preponderating reaction or that which for the purpose in view is of chief interest. In order to write an equation the nature of the substances added to one another must be known and the nature of all the substances produced. These equations are quantitative expressions and the sum of the weights of the molecules entering into the reaction (factors) must be equal to the sum of the weights of the resulting molecules (products) ; that is, no material is ever lost or created in a reaction. It must be borne in mind that these equations are a species of chemical shorthand and are imperfect, leaving unexpressed much that is of importance and interest in regard to the changes represented.

Experiment 13.—Weigh out 2 grams of lead nitrate ($Pb(NO_3)_2$) and 1.06 grams potassium sulphate (K_2SO_4). Dissolve each salt in water and after heating each solution to boiling, mix them slowly with constant stirring. When somewhat cooled, add one-fourth as much alcohol and stir. After standing twenty-four hours, filter and wash the precipitate of lead sulphate twice with alcohol. Dry the precipitate in the steam-closet and weigh on the filter-paper, taring with a filter-paper of the same size on the other pan. Evaporate the filtrate on a water-bath to dryness in a small weighed porcelain dish, and heat in the steam-closet. Weigh the potassium nitrate formed.

$$Pb(NO_3)_2 + K_2SO_4 = PbSO_4 + 2KNO_3$$

<pre>
207 14 16   39 32 16   207 32 16   39 14 16
          3   2   4   4   3
         ‾‾   ‾‾   ‾‾   ‾‾   ‾‾
         48   78   64   64   48
        ‾‾‾   ‾‾‾‾‾‾   ‾‾‾   ‾‾‾
         62   174   303   101
          2   2
        ‾‾‾   ‾‾
        124
       ‾‾‾‾‾
        331   202
     ‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾   ‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾
            505.   505.
</pre>

How much of each element was concerned in the reaction?

As an example of chemical equation we may take the change taking place when barium chlorid and sulphuric acid are brought into contact with one another.

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$
$$137 + (2 \times 35.5) + (2 \times 1) + 32 + (4 \times 16) = 137 + 32 + (4 \times 16) + 2 \times (1 + 35.5) = 306.$$
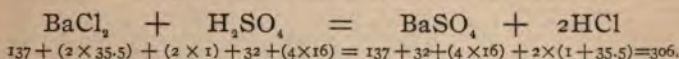
For convenience, reactions are divided into four classes.

a. Analysis.—This is a change in which a molecule is separated into its elements or into simpler molecules. The decomposition of water into hydrogen and oxygen is a case of analysis.

$$2H_2O = 2H_2 + O_2.$$
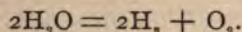
Similarly the decomposition of limestone into calcium oxid and carbon dioxid is analysis.

$$CaCO_3 = CaO + CO_2.$$
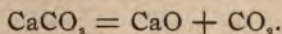
Experiment 14.—Decompose water, slightly acidulated with sulphuric acid, by electricity. A satisfactory electrode may be made by folding one end of a strip of platinum foil, 5×1 cm., about a copper wire, passing the wire through a glass tube and sealing the junction of the platinum and wire into the end of the tube. The tube may be subsequently so bent as to hang over the edge of a beaker in which the water is decomposed and the gases may be collected by inverting test-tubes over the electrodes. Notice the relative quantities of oxygen and hydrogen formed.

Experiment 15.—Heat potassium chlorate ($KClO_3$) in a closed tube and test the oxygen (O_2) evolved, by a spark on a splinter of wood. After the gas ceases to be evolved, break the tube and taste the potassium chlorid (KCl) remaining in the tube, comparing it with the taste of the potassium chlorate used.

b. Synthesis.—This is where elements are united into compounds or simple molecules into more complex ones. When copper and sulphur are heated together they unite to form copper sulphid.

$$Cu + S = CuS.$$
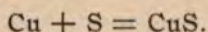
When carbon dioxid is absorbed by calcium oxid, forming calcium carbonate, we have the reverse of the preceding case of analysis or synthesis.

$$CaO + CO_2 = CaCO_3.$$
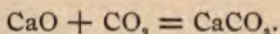
Experiment 16.—Rub together in a mortar small quantities of mercury (Hg) and iodin (I), moistening the mixture with a few drops of alcohol (C_2H_5OH).

a. Conduct carbon dioxid (CO_2) into lime-water. By blowing through a tube into lime-water, the carbon dioxid (CO_2) exhaled from the lungs unites with the dissolved lime (CaO), and calcium carbonate ($CaCO_3$) is precipitated.

c. Substitution.—Where an element is substituted for another in a molecule, as when a metal reacts upon an acid replacing the hydrogen of the acid, we have an instance of this kind of chemical change.

$$Fe + 2HCl = FeCl_2 + H_2.$$
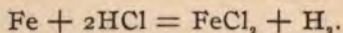
Experiment 17.—Place a piece of iron in a solution of copper sulphate ($CuSO_4$). The next day test the solution with potassium ferrocyanid ($K_4Fe(CN)_6$), and compare with the action of this reagent on the original copper sulphate solution.

Experiment 18.—Treat hydrochloric acid (HCl) with zinc (Zn). Notice the gas given off and test its combustibility.

d. Double Decomposition.—This is a chemical reaction in which the elements or groups of elements in different

molecules exchange places, as when lead nitrate and potassium sulphate are mixed we get lead sulphate and potassium nitrate.

$$Pb(NO_3)_2 + K_2SO_4 = PbSO_4 + 2KNO_3.$$
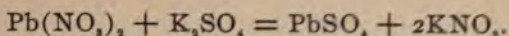
Experiment 19.—To 5 cc. of a solution of barium chlorid $(BaCl_2)$ in a test-tube, add an equal quantity of a solution of potassium sulphate (K_2SO_4). Let the precipitated barium sulphate $(BaSO_4)$ settle and evaporate some of the supernatant liquid which contains the potassium chlorid (KCl) formed.

Experiment 20.—Add, as above, a solution of sodium hydroxid $(NaOH)$ to one of copper sulphate $(CuSO_4)$.

Experiment 21.—Add, as above, a solution of ammonium carbonate $((NH_4)_2CO_3)$ to one of calcium chlorid $(CaCl_2)$.

43. Conditions Favorable to Chemical Reaction.—In order that chemical reaction may take place between molecules they must be at insensible distances from one another. Hence it follows that the solid state is unfavorable for reactions. Solids can be made to react upon one another by exerting great pressure upon them and thus bringing the molecules much closer. The liquid or the gaseous state, where there is more freedom of movement, is more favorable to reaction. Similarly higher temperatures where there is more rapid motion, favor the more speedy mingling of the unlike molecules and contribute to the energy of the reaction. This motion must not, however, in general, be too rapid, as this increased motion may overcome the affinity of the atoms. While in many cases the gaseous state is the most favorable for chemical reaction, yet for convenience the liquid state is the one most frequently used in actual practice. By far the largest number of solid reagents are used in the form of aqueous solutions and many gases are also often used in solution, as hydrogen chlorid, hydrogen sulphid, ammonia, sulphur dioxid, etc.

Experiment 22.—Mix together copper filings and sulphur. Heat the mixture in a tube—

a. Mix together crystals of copper sulphate ($CuSO_4$) and potassium ferrocyanid ($K_4Fe(CN)_6$).

b. Grind the two salts together in a mortar.

*c*. Add a solution of potassium ferrocyanid ($K_4Fe(CN)_6$) to one of copper sulphate ($CuSO_4$).

Compare *a*, *b*, and *c*.

44. Correlation of Chemical and Physical Forces.— In no chemical reaction is chemical force the only one concerned. Heat, light, and electricity may be the cause of chemical action, and chemical action is always accompanied by heat (evolution or absorption) and probably always by electricity, and often by light and even sound. While it might seem desirable that the science of chemistry should concern itself only with the action of chemical force—chemical affinity—and the factors and products of such action, so closely are the physical and chemical forces intertwined at every point, that such restriction is not only undesirable but would be impossible. More and more is the chemist concerning himself with the physical side of his science and the division of physical chemistry is becoming one of the most important branches of the science.

45. Thermochemical Phenomena.—We have seen that every chemical reaction is accompanied by evolution or absorption of heat. Reactions in which heat is evolved are *exothermic*; those in which heat is absorbed are *endothermic*. As an example of an exothermic reaction we have the union of oxygen and hydrogen to form water. We should express this in an equation thus :

$$2H + O = H_2O + 68000 \text{ calories.}$$
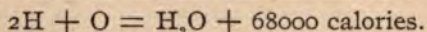
(The calorie is the unit of heat, *i. e.*, the amount required to raise one gram of water from $0°$ to $1°$ C.) Some-

times the great calorie, the amount of heat required to raise 1 kilo of water from 0° to 1° C. is used as the unit. The equation would then be

$$2H + O = H_2O + 68 \text{ great calories.}$$
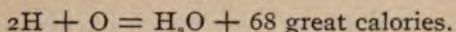
The formation of hydrogen iodid is an endothermic reaction and would be expressed by the equation

$$H + I = HI - 7000 \text{ calories.}$$
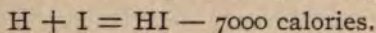
46. Exothermic Compounds.—A compound formed by an exothermic reaction is an exothermic compound and possesses less energy than its constitutents and is more stable than the mixture of its constituents, as it can be separated into its constituents only by the addition of energy. Heat is often necessary to start an exothermic reaction, it being necessary to weaken the attraction between the atoms of the molecules of the constituents ; but, once started, the heat evolved is sufficient for this, and the reaction proceeds of itself, often with explosive rapidity ; conversely, exothermic compounds can be decomposed only by the addition of such energy as was evolved in their formation.

47. Endothermic Compounds.—Endothermic compounds possess more energy than their constituents and are unstable, decomposing into their constituents with an evolution of energy (heat). In endothermic compounds, given an external impulse, the decomposition proceeds of itself. Most explosive compounds are endothermic.

48. Conditions of Reaction in Double Decomposition.— According to the theory of solutions at present most favored among chemists, the following would be the explanation of the changes taking place in double decomposition :

When salts (including hydrogen salts or acids) are

dissolved in water, we may consider a part of the positive and the negative portions (or ions) of the salt separately in solution. Thus in a solution of copper sulphate ($CuSO_4$), we would have separately in solution the ions (Cu) and (SO_4); in the case of nitric acid (HNO_3) we would have (H) and (NO_3). If now we have two salts in solution and one of the positive ions forms with a negative ion a substance insoluble in water, this substance will be precipitated until all of one of its component ions have been removed from solution. Thus if we dissolve in water lead nitrate ($Pb(NO_3)_2$) and add to it a solution of sodium sulphate (Na_2SO_4) we would have in solution the positive ions (Pb) and (Na) and the negative ions (NO_3) and (SO_4). Now since the compound ($PbSO_4$) is insoluble in water, it will be precipitated until the supply of (Pb) or of (SO_4) in the solution has been exhausted.

Similarly if we have, in solution, ions which could form water and a gas, the reaction will take place and the gas escape except in so far as it is soluble in the liquid at the temperature of the reaction. Thus if we mix solutions containing sodium carbonate (Na_2CO_3) and hydrochloric acid (HCl), the ions are (Na) and (H) positive and (CO_3) and (Cl) negative. But carbonic acid (H_2CO_3) is composed of water (H_2O) and carbon dioxid (CO_2) a gas. This gas therefore escapes.

If we mix solutions of ammonium chlorid (NH_4Cl) and potassium hydroxid (KOH), the ions are (NH_4) and (K) positive and (Cl) and (OH) negative. But ammonium hydroxid (NH_4OH) is composed of water and ammonia (NH_3) gas. At ordinary temperatures ammonia is very soluble in water, hence none escapes. But by heating the water, ammonia, being less soluble in hot water, escapes and at 100° may be completely

removed from the solution, provided the requisite (equivalent) quantity of KOH, and hence (OH), is present.

49. This Introduction Contains, in outline, some of the great principles of the science. It is scarcely expected that they will be fully grasped and comprehended by the student just entering upon the study. He is rather to look upon much of it as a statement of what is to be proved by his further study. A good deal of it will be repeated in suitable places later when facts have been acquired which will render explanation possible. It is scarcely practicable to start upon the study of the science without some such framework for the building.

PART II

THE ELEMENTS

It has been stated that there are seventy or more different elements in nature and out of these all the different kinds of matter are formed. A thorough knowledge of these elements and of their distinguishing properties is necessary before their combinations can be studied. To get a complete picture of these elements we must also know something as to their occurrence in nature, their relative abundance and importance, and have a brief account of how they become known to man. The Periodic Table, as given, will be closely followed. The standard element, hydrogen, will be first considered.

Hydrogen

SYMBOL, H.   ATOMIC WEIGHT 1.008.   VALENCE 1.

50. History.—As early as the sixteenth century Paracelsus made mention of the production of an inflammable gas by the action of dilute acids upon certain metals. It was Cavendish, however, who in 1766 first found out something of the nature of this gas, giving it the name "inflammable air." In the year 1781 he showed that water was formed by the union of this inflammable air with oxygen. The great importance of this discovery impressed itself upon Lavoisier who studied the nature of this gas and gave it the name hydrogen or the generator of water.

51. Occurrence.—1. *Free or Uncombined.*—While traces of hydrogen may be found uncombined upon the earth, as in volcanic gases, such occurrence is rare and unimportant. Its nature and affinity for oxygen would forbid its free occurrence in the atmosphere or rather its remaining there any length of time. In the atmospheres of the sun and other celestial bodies it is very abundant in the free condition.

2. *Combined.*—Hydrogen is combined with oxygen in water, forming one-ninth of its weight; with carbon and oxygen in all organic matter; it is also a constituent of all acids.

52. Preparation.—1. *From Water.*—*a.* By decomposing water by electricity. When an electric current is passed through water, which has been slightly acidulated to make it a good conductor, the water is decomposed and the hydrogen seeks the negative pole while the oxygen goes to the positive. This reaction would be expressed by the equation:

$$2H_2O = 2H_2 + O_2.$$
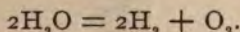
b. By the action of certain metals upon water. These metals have the power of decomposing water, combining with the oxygen, and setting all or a part of the hydrogen free. In some cases the action will take place at ordinary temperatures, as with potassium or sodium; again with others a high temperature is necessary, as with zinc or iron.

Fig. 2.
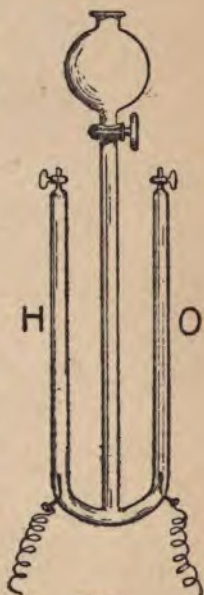
$$2Na + 2H_2O = 2NaOH + H_2$$
$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$
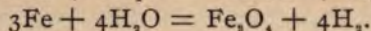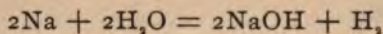
In the cases of potassium and sodium (if in large amount or if kept in one spot), the heat evolved is sufficient to set on fire the hydrogen liberated.

2. *From Acids.*—When some acids are acted upon by metals, substitution takes place, a salt being formed and hydrogen evolved. This is the usual method of obtaining hydrogen, the most frequently used acid and metal
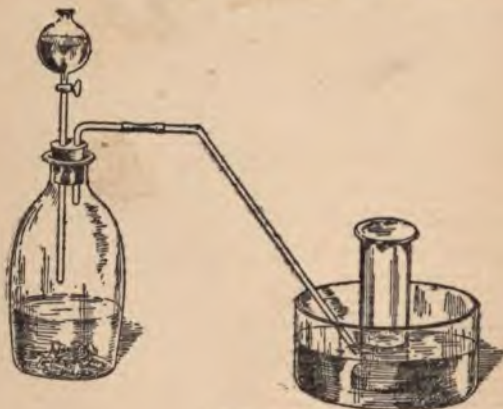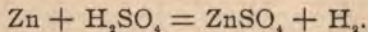

Fig. 3.

being sulphuric acid and zinc. The acid must be considerably diluted so that the water may dissolve the zinc sulphate formed and prevent its covering over and protecting the zinc from further action.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

53. Properties.—Hydrogen is a colorless, odorless, tasteless gas. It is only slightly soluble in water and so can be collected over a pneumatic trough. It is the lightest substance known and therefore, if caught by

displacement, the collecting vessel must be held mouth
downwards.   Compared with air it is 14.39 times lighter.
Hence its specific gravity is 0.06949. One liter of
hydrogen weighs 0.08987 gram. This number is of
importance since by multiplying it by the density (half
the molecular weight) of any gas we obtain the weight
of a liter of that gas. We have good reasons for
believing that the hydrogen molecule is made up of two
atoms. Hydrogen has not as yet been condensed to a
stable liquid as it has not hitherto been possible to reduce
it to a temperature below its critical point. It is used
in thermometers for measuring very low and very high
temperatures. The properties just given are called
the physical properties.

54. Chemical Properties.—Examining hydrogen as to
its chemical properties, we find that a taper plunged
into it is extinguished. It is therefore not a supporter
of combustion in the sense in which that term is com-
monly used.   It is, however, combustible, burning
either in oxygen or air. The flame is colorless and the
heat evolved very great, greater than by any other
combustion.

$$2H_2 + O_2 = 2H_2O.$$
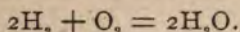
Combustion, or the union with oxygen, is known as
an oxidation process. Hydrogen shows an especial
affinity for the more negative elements as chlorin,
nitrogen, and carbon. Its strong affinity for oxygen and
chlorin causes it to unite with explosive violence when
mixed with either of them and brought under the proper
conditions for combination. In the case of oxygen it
must be heated to what is called the kindling tempera-
ture or ignition-point : in the case of chlorin the reac-
tion takes place when the mixed gases are exposed to

some strong and active light. With carbon it forms a very numerous class of bodies called the hydrocarbons. It shows very little tendency to unite with the positive elements, though it can be made to unite with some of them indirectly. Some of the elements, as platinum and palladium, have the power of absorbing and condensing hydrogen; thus one volume of palladium can condense 982 volumes of hydrogen. The latent heat rendered sensible in this change from the gaseous to a solid state is sufficient to cause it to unite with oxygen. On this principle a lamp was constructed many years ago by Döbereiner. He let a stream of hydrogen fall upon a piece of finely divided " spongy" platinum. If the platinum was clean and perfectly dry the hydrogen caught on fire and other objects could be ignited by means of it. The intense heat given off by the combustion of hydrogen is utilized by means of the oxyhydrogen lamp in which the oxygen and hydrogen are united and burned just at the point of exit. This is used in the lime light, lead burning, for smelting platinum, etc. On account of its lightness hydrogen is also used for inflating balloons. When pure, hydrogen may be breathed for a short time without injury. It has a singular effect upon the voice, weakening it and giving it a higher pitch.

Experiment 23.—Throw a small piece (half the size of a pea) of potassium (K) on water. Do the same with sodium (Na), and note the difference. Set fire to the gas evolved when sodium is used. Warm water in a porcelain dish and throw on a small piece of sodium. Feel the water with the fingers. Test it with litmus paper.

Experiment 24.—Collect the gas evolved from the action of sodium on water by holding the sodium wrapped in wire gauze under an inverted test-tube filled with water in the pneumatic trough. Test the inflammability of the gas by holding the mouth of the test-tube to a flame.

Experiment 25.—Make hydrogen in a test-tube fitted with a delivery-tube, by the action of iron (Fe) on hydrochloric acid (HCl);
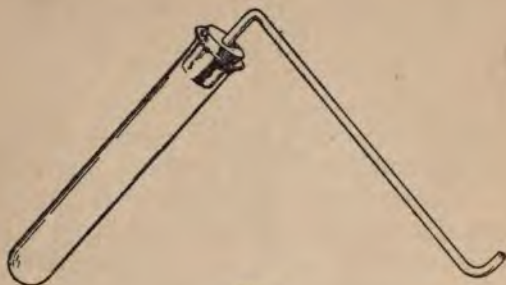

Fig. 4.

iron (Fe) on sulphuric acid (H_2SO_4); zinc (Zn) on hydrochloric acid (HCl); and zinc (Zn) on sulphuric acid. In each case test the hydrogen as to inflammability, and in the case in which it is most copiously evolved, as to lightness, by pouring *upward* into another test-tube and testing for its presence by applying a flame.

Experiment 26.—Fill two tubes with hydrogen and expose each for a minute (or two), one held upright and the other inverted, and then test for hydrogen in each with a flame. From which does it escape most rapidly, and why?

Experiment 27.—Fill a wide-mouthed bottle with hydrogen and keeping it inverted, insert a lighted candle or taper, then slowly withdraw the candle. What does this experiment prove as to combustibility of hydrogen, and as to hydrogen as a supporter of combustion?

Fig. 5.

Experiment 28.—Burn a small jet of hydrogen in a dry bell jar. What is formed and why?

GROUP VII

F 19.06
|
Cl 35.45
∧
Br 79.95
|
I 126.85
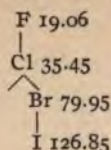
It will be better now to begin the study of the remaining elements of the table with Group VII, taking the groups in order from right to left. We will study first the group element, then the type, and then the two subseries beginning with the negative subseries on the negative side and with the positive subseries when the positive side of the table has been reached. While the elements of each group resemble each other in many respects, the '' group element,'' which is the member of each group having the lowest atomic weight, deviates from the general properties of the members of the group more than the other elements differ from each other, hence it is the second element of each group that is considered the representative one and is the '' type element.'' The '' group element'' may also be called the '' bridge element'' as it seems to serve as a connecting link with the next group and presents some of the properties exhibited there.

55. General Characteristics of the Seventh Group.— These elements are all strongly negative and combine readily with those more positive. (Manganese belonging to the positive subseries will be considered later.) Owing to their strong affinities they do not occur in nature uncombined but are found in binary compounds with the positive elements and, with the exception of fluorin, are commonly found together. Chlorin is the most abundant and the abundance of the others rapidly

falls off with increase of atomic weight. A distinct gradation of properties is to be observed between these elements, depending upon the increase in atomic weight. Bromin has an atomic weight which is almost exactly the mean of those of chlorin and iodin, and its properties are also a mean between those of the other two elements. The negative character and chemical activity decrease with the increase of atomic weight. These elements all have a valence of one towards hydrogen ; that is, they combine atom for atom with that element. The group is said to be univalent. Towards oxygen the valence may be as high as seven. It should be noticed that this corresponds with the position and number of the group.

Fluorin

SYMBOL F.   ATOMIC WEIGHT 19.06.   GROUP ELEMENT.

56. History.—While this element was known in its compounds for a very long time it proved impossible to separate and isolate it on account of its very active properties. It was first prepared by Moissan in 1886, by the decomposition of hydrofluoric acid by means of electricity. For this purpose it was necessary to use vessels made of platinum and fluor spar, as other materials were rapidly attacked by free fluorin.

57. Occurrence.—*Always combined*. The most abundant compound is the one with calcium, CaF_2. This is known as fluor spar, or fluorite, and is quite widely distributed. It is from this compound that the name of the element is derived. Cryolite, a fluorid of aluminum and sodium (AlF_3, $3NaF$), occurs in Greenland. It is found in small amounts in the bones of animals and in the enamel of the teeth.

58. Properties.—This is a nearly colorless gas, heavier than air. It does not burn in air. It has been condensed to a light yellow liquid. It is one of the most energetic elements known, intensely negative. It decomposes water, combining with the hydrogen, and attacks all compounds of silicon, as glass and porcelain, combining with the silicon.

Fluorin for a long time has been supposed to form no compound with oxygen, and there is still no positive proof of the formation of such a compound. Fluorin acts most destructively upon organic matter, and so is very dangerous to life.

Chlorin

SYMBOL Cl.   ATOMIC WEIGHT 35.45.   TYPE ELEMENT.

59. History.—In 1774 Scheele first prepared chlorin by the action of hydrochloric acid upon manganese dioxid. He called it '' dephlogisticated marine acid gas.'' For many years it was regarded as a compound of hydrochloric acid with oxygen but in 1810 Davy showed that it was an element and gave it the name which it now bears ($\chi\lambda\omega\rho\acute{o}s$, greenish yellow).

60. Occurrence.—*Always combined*. Its most abundant compound is with sodium in what is known as common salt. This is found on the earth in immense quantities and very widely distributed. Compounds with potassium, magnesium, calcium, and other metals are also met with.

61. Preparation.—*a*. Chlorin may be obtained by the action of sulphuric acid upon manganese dioxid and sodium chlorid.

$$2NaCl+MnO_2+2H_2SO_4=Na_2SO_4+MnSO_4+2H_2O \quad Cl_2.$$
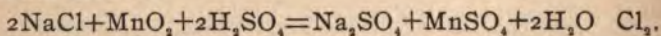
b. By the action of hydrochloric acid upon manganese dioxid (this is in reality a part of the first reaction).

$$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2.$$
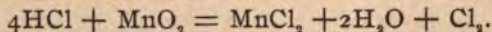
c. For commercial purposes chlorin is sometimes prepared by the oxidation of the hydrogen in hydrochloric acid by passing it along with air over clay balls saturated with copper sulphate.

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$
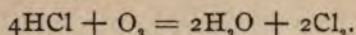
62. Properties.—It is a greenish-yellow gas with a disagreeable and suffocating smell. It is heavier than air (sp. gr. 2.45) and easily condensed to a yellow liquid (pressure of 6 atmospheres at the ordinary temperature). This liquid is one-third heavier than water. It is readily soluble in water. As the chlorin slowly decomposes water, the solution cannot be preserved very long. By cooling the solution crystals of a compound with water (a chlorin hydrate) can be obtained. Chlorin is not combustible, nor does it combine readily with oxygen. With many positive elements chlorin unites with great energy. Thus with hydrogen it unites with explosive violence when a mixture of the two gases is exposed to bright light. Sodium, copper, and a number of similar elements burn brilliantly in an atmosphere of chlorin gas. It has a powerful bleaching action upon vegetable colors. In bleaching, the objects of the action should be wet. The chlorin decomposes the water, taking the hydrogen, forming with it hydrochloric acid, and setting the oxygen free. This nascent oxygen oxidizes the coloring-matter. Chlorin can also remove hydrogen directly from the organic matter, thus destroying it. It is an energetic disinfectant, though it is too powerful to be used directly in most cases. Chlorin and water are frequently used for oxidizing purposes. Though chlorin does not unite directly with oxygen and shows comparatively little affinity for it, it forms several compounds with it. These are unstable and easily decomposed. It is an

irritant poison, speedily causing death when breathed.

Bromin

SYMBOL Br.   ATOMIC WEIGHT 79.95.

63. History.—This element was discovered in 1826 by Balard.

64. Occurrence.—It is found combined with the same elements as chlorin and generally along with the compounds of chlorin, though far less abundant. It is most commonly found combined with sodium or potassium.

65. Preparation.—The potassium or sodium compound can be heated with manganese dioxid and sulphuric acid.

$$2NaBr + MnO_2 + 2H_2SO_4 =$$
$$Na_2SO_4 + MnSO_4 + 2H_2O + Br_2.$$
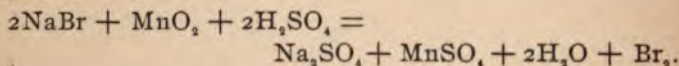
Or these compounds may be treated with chlorin.

$$NaBr + Cl = NaCl + Br.$$
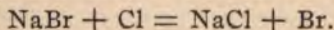
66. Properties.—It is a heavy, dark red liquid, with a disagreeable suffocating smell. At —22° it freezes to a solid and at 63° it boils. Its specific gravity is 3.18. It is somewhat soluble in water. It is not combustible. The vapor combines with hydrogen when heated. It is an energetic negative element, though less so than chlorin, and can be displaced from its compounds with the positive elements by chlorin. It bleaches and can be used as a disinfectant. The vapors when inhaled produce great irritation and affect the eyes very painfully. Like chlorin it is an irritant poison when swallowed, and it produces a sore upon the skin which is difficult to heal. With water it gives a crystalline hydrate upon cooling. It slowly decomposes water upon exposure to sunlight, liberating oxygen.

Iodín

67. History.—Iodin was discovered in 1811 by a French soap-maker, Courtois, in soda from the ash of seaweeds used in making soap.

68. Occurrence.—Iodin is chiefly found in sea-water (combined probably with calcium and oxygen) and in certain springs in combination with potassium or sodium. It is obtained largely from the ash of seaweeds, and from Chile nitre.

69. Preparation.—*a*. Potassium iodid is heated with manganese dioxid and sulphuric acid.

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2.$$
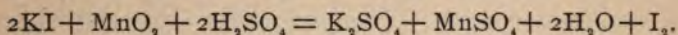
b. Or the solution of potassium iodid is treated with chlorin and the liberated iodin precipitated or dissolved out by means of ether.

$$KI + Cl = KCl + I.$$
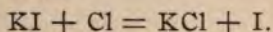
70. Properties.—Iodin is a crystalline gray solid having a specific gravity of 4.948 and melting at 113°. It boils above 200° giving a heavy vapor of a deep blue or violet color. It is only slightly soluble in water but is easily dissolved by alcohol, ether, carbon bisulphid, or a solution of potassium iodid.

Chemically it resembles chlorin and bromin. These two have the power of displacing it from its compounds with the positive elements but the reverse is the case in reference to compounds with oxygen. It has a slight bleaching action. Its most characteristic property is the formation of a splendid blue color with starch paste. Like the preceding elements this is an irritant poison. It is frequently used medicinally in the form of a solution in

alcohol. Its binary compounds with the positive elements are called iodids.

These elements are called the *halogens* or salt-makers. The gradation in their properties is best exhibited in tabular form.

PROPERTIES OF THE HALOGENS.

Properties.	Fluorin.	Chlorin.	Bromin.	Iodin.
Atomic weight.	19.06	35.45	79.95	126.85
Physical state..	gas	gas	liquid	solid
Color..........	faint yellow	greenish yellow	brown-red	gray
Melting-point..	......	-102°	-22°	113°
Boiling-point ..	-183°	-33.6°	63°	200°
Specific gravity	1.14	1.33	3.18	4.95
Specific gravity of vapor (air=1)	1.31	2.45	5.53	8.7

Experiment 29.—Mix equal parts common salt (NaCl) and manganese dioxid (MnO_2) in a test-tube (about 5 grams in all);

add two or three cc. of water and then very carefully twice as much *concentrated* sulphuric acid (H_2SO_4). Examine the evolved gas as to color, odor, etc. Hold a moistened piece of colored cloth in the test-tube.

Experiment 30. — Generate chlorin (Cl) by the action of manganese dioxid (MnO_2) on concentrated hydrochloric acid (HCl). Try also the effect of chlorin on a colored flower. The manganese dioxid and hydrochloric acid are put in the flask provided with a safety funnel. The chlorin coming off is washed by passing through the wash-bottle half full of water.

Fig. 6.

Experiment 31.—Generate bromin (Br) by the action of sul-

phuric acid (H_2SO_4) on a mixture of potassium bromid (KBr) and manganese dioxid (MnO_2). Generate iodin (I) by the action of sulphuric acid on a mixture of potassium iodid (KI) and manganese dioxid (MnO_2). In these two experiments use about a gram of the potassium salt. Note the physical properties of the bromin and iodin, and compare with chlorin.

Experiment 32.—Obtain bromin (Br) by treating a solution of potassium bromid (KBr) with chlorin (Cl) water.

Experiment 33.—Obtain iodin (I) by treating a solution of potassium iodid (KI) with chlorin (Cl) water. In both of these cases divide the solution and shake one portion with carbon bisulphid (CS_2), and to the other add a few drops of boiled starch.

Experiment 34.—Dissolve a little iodin (I) in alcohol; in water; add a bit of potassium iodid (KI) to the water.

Experiment 35.—Warm a few crystals of iodin (I) in a dry test-tube.

GROUP VI

O 16
|
S 32.07
/\
52.14 Cr   Se 79.02
| |
95.99 Mo   Te 127.49
|
184.83 W
|
239.59 Ur
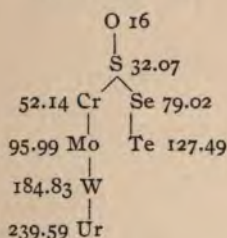
For the present, the discussion of series I will be omitted. The elements of this group are all bivalent to hydrogen, forming the compounds H_2O, H_2S, H_2Se, and H_2Te. Towards oxygen they are quadrivalent or sexivalent, forming OO_2, SO_2, SO_3 ; SeO_2 SeO_3, TeO_2, TeO_3. They are less strongly negative than the elements of the seventh group. There is comparatively little affinity exhibited between the elements of the two groups.

Oxygen

SYMBOL O. ATOMIC WEIGHT 16. GROUP ELEMENT.

71. History.—One hundred years before the discovery of oxygen in the real sense of the term, certain chemists of the 17th century, Hooke, Mayow, and Boyle, had prepared a gas by the heating of nitre and examined into some of its properties. Near the middle of the 18th century Scheele also prepared this gas from nitre but it was not until 1775 that the gas was properly isolated and recognized by Priestley who obtained it by heating mercuric oxid and called it "dephlogisticated air." At very nearly the same time Scheele discovered it independently, obtaining it from manganese dioxid. The value of this great discovery was understood by Lavoisier, and he studied the gas more fully and named it oxygen, under the impression that it was essential to all acids and so was the acid-maker (the derivation is from the Greek ὀξύς γέν ναω).

72. Occurrence.—1. *Free*, in the atmosphere of which it forms about one-fifth by volume or one-fourth by weight, being mixed with nitrogen.

2. *Combined* with various elements, forming oxids, as water (H_2O), silica (SiO_2), zinc oxid (ZnO), and ferric oxid (Fe_2O_3) ; secondly with groups of positive and negative elements forming salts, as calcium carbonate, barium sulphate, magnesium silicate, etc. Oxygen is also a component of most animal and vegetable substances being in this case combined with carbon and hydrogen. It is the most abundant of the elements and forms about one-half of all the matter upon the earth's surface.

73. Preparation.—1. By passing the electric current through water (slightly acidulated to render it conduct-

ing) the two elements are separated and may be collected, the oxygen at the positive and the hydrogen at the negative electrode.

$$H_2O = H_2 + O.$$
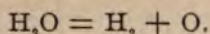
2. Again it may be prepared by heating certain oxids as mercuric oxid or manganese dioxid.

$$2HgO = 2Hg + O_2.$$
$$3MnO_2 = Mn_3O_4 + O_2.$$
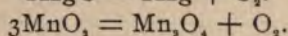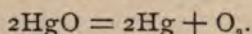
3. Or by heating certain salts as potassium nitrate, or potassium chlorate. The latter is the usual method. The potassium chlorate may be heated in a tube (Fig. 4), and the gas caught in jars over water.

$$2KClO_3 = 2KCl + 3O_2.$$
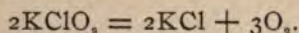
On a larger scale a mixture of potassium chlorate and manganese dioxid is heated in a copper retort so as to cause the oxygen to come off at a lower temperature and more regularly.

74. Properties.—A colorless, odorless, tasteless gas, a little heavier than air (sp. gr. 1.10562). One liter of it at 0° and 760 mm. pressure weighs 1.429 grams. It can be condensed to a liquid by pressure at a very low temperature. This liquid is a little more than half as heavy as water. Oxygen dissolves appreciably in water. It is a supporter of combustion and the fact that the atmosphere supports combustion is due to its presence. It forms compounds with all the elements (though fluorin and bromin oxids have not yet been isolated and examined). These compounds are called oxids.

The combustion processes are among the most important in nature. The false theories as to their nature retarded the progress of the science. With the discovery of oxygen and its properties the explanation of these

processes was made clear. Combustion in pure oxygen is very much more brilliant and rapid than in the diluted oxygen of the air. Oxygen can be breathed in the pure state for a time without injury and is made use of by physicians in some cases of weakened lung action. Respiration and decay are combustion processes. Sometimes the action is slow but the heat evolved is always the same whether the action be slow or rapid.

Experiment 36.—Heat mercuric oxid (HgO) in a closed tube. Test the evolved gas with a spark. What is left in the test-tube? Write the reaction.

Experiment 37.—Heat potassium chlorate (KClO₃) in a closed tube. Test the gas. What is left ?

Experiment 38.—Fit a cork and a delivery-tube to a test-tube. In the (dry) test-tube, heat gently a mixture of about five grams, or less, of potassium chlorate (KClO₃) and one gram of manganese dioxid (MnO₂). Collect the evolved gas in inverted test-tubes or bottles, filled with water over the pneumatic trough. With the gas so obtained (and with that from the oxygen cylinder) perform the following experiments.

Experiment 39.—*a.* Insert a stick with a glowing spark. *b.* Insert a piece of ignited sulphur in a deflagrating spoon. *c.* Insert a piece of phosphorus (*cut it under water !*). Note the difference between combination in air and in oxygen. *d.* Wrap a bit of string about the end of a steel watch-spring, coat it with melted sulphur, and having ignited it insert it in a bottle of oxygen. (Have wet oakum in the bottom of the bottle.) *e.* Insert a piece of ignited charcoal in a deflagrating spoon.

Ozone

SYMBOL O₃. MOLECULAR WEIGHT 48.

75. Ozone.—More than a hundred years ago it was known that oxygen, through which an electric spark had been passed, possessed a peculiar odor. It was not until 1840, however, that the cause of this was pointed out by Schönbein. He gave the name of ozone (from ὄζω,

I smell) to this peculiarly smelling substance. It has been shown to be another form of oxygen. When an element exists in two or more different forms, these are called *allotropic* states or modifications.

Ozone may be formed by the passage of electricity through moist oxygen. Thus it is formed in the passage of lightning through the atmosphere. Also by the life action of plants, the oxygen given off by the leaves containing some ozone. It may be obtained by the slow oxidation of phosphorus and is formed in a number of other processes of slow oxidation.

Ozone is denser than oxygen, being half again as heavy. It is somewhat soluble in water and more so in ether. The water has its peculiar odor and its other characteristic properties. By heating to about 300° it is changed back into oxygen. It has very strong oxidizing powers, oxidizing some bodies not affected by ordinary oxygen. Hence for some time it was known as active oxygen. It will oxidize such bodies as silver, rubber, etc. In the atmosphere it oxidizes and destroys organisms and other organic matter, thus aiding in purifying the air. It is used commercially in some oxidizing processes.

The theory is that this form of oxygen has three atoms in the molecule, whereas the ordinary oxygen has only two. Ozone is unstable and easily breaks up into ordinary oxygen and a single atom oxygen, the latter having strong oxidizing power and the general chemical energy of nascent oxygen.

Its formula may be represented as $O=O^{IV}=O$ or $\begin{smallmatrix} & O & \\ \diagup & & \diagdown \\ O & \!\!-\!\! & O \end{smallmatrix}$ the formula for ordinary oxygen being $O=O$ and for nascent oxygen $-O-$.

Sulphur

SYMBOL S. ATOMIC WEIGHT 32.07. TYPE ELEMENT.

76. Occurrence.—Sulphur occurs free and has been known from very early times. It is usually found in the neighborhood of volcanoes. A great deal of the world's supply of sulphur comes from Mt. Etna in Sicily. It is also very abundant and widely distributed in the combined condition. It may be combined with positive
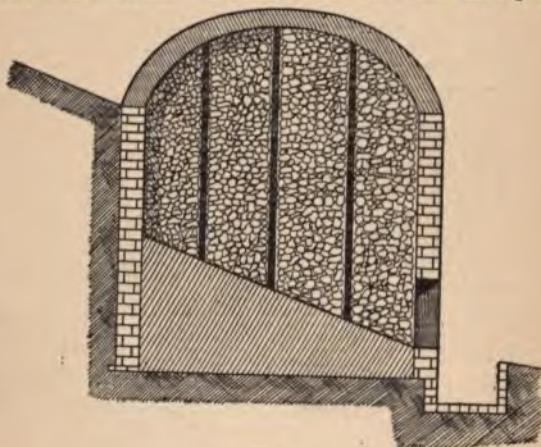
Fig. 7.

elements as iron (pyrites, FeS_2); lead (galena, PbS); zinc (blende, ZnS); etc. Or it may be combined with oxygen and some positive element, as calcium in gypsum, $CaSO_4$. Sulphur is to be classed among the abundant elements but the total amount is very much less than that of oxygen.

77. Preparation.—It is chiefly obtained from the native sulphur by collecting the sulphur mixed with gangue and melting the sulphur off in kilns (see Fig. 7). This crude sulphur is then purified by melting

again, distilling and casting in wooden molds, or by forcing it as vapor into large chambers where it is condensed as a fine yellow powder (Fig. 8). This latter form is called
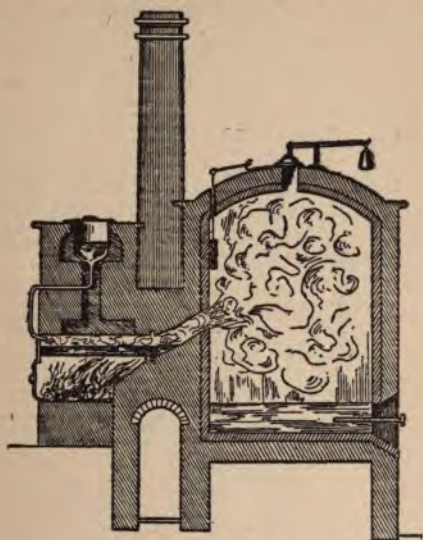
Fig. 8.

flowers of sulphur. The stick-like pieces obtained from the molds are known as roll sulphur or brimstone. These are the commercial forms. Sulphur is also obtained in smaller quantities by heating certain of the natural metallic sulphids as iron pyrites, without exposure to air.

78. Properties.—Sulphur is, at ordinary temperatures, a yellow, almost odorless, brittle solid, having the specific gravity 1.8 and melting at 115° to a thin amber liquid. When heated to a higher temperature it grows darker and becomes thick and viscid, still higher it grows thinner and at 450° it boils, giving off a yellowish brown vapor of a high density. It is insoluble in water,

but is soluble in sulphur chlorid and some forms of it are soluble in carbon bisulphid.

At 500°, the density is 124 corresponding to the molecule S_8; only above 1000° does its density become 32 corresponding to the molecule S_2. Nothing is known of

Fig. 9.

Fig. 10.

the number of atoms in the molecule of solid sulphur. It is strongly negative, combining with the positive elements, forming compounds known as sulphids. It burns with a blue flame in oxygen or air, giving off white fumes of sulphur dioxid.

$$S + O_2 = SO_2.$$
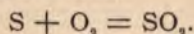
Sulphur exists in several allotropic modifications.

1. *Rhombic Sulphur.*—This is the ordinary and stable form. The native crystals are in this form and so too the sulphur crystallized from solutions in carbon bisulphid (Fig. 9).

2. *Monoclinic Sulphur.*—This is formed when sulphur cools slowly from a fused condition. The crystals are long, transparent, and needle-like (Fig. 10). It changes into the first form on standing.

3. *Plastic Sulphur—An Insoluble Form of Sulphur.*— This form is obtained when sulphur, near the boiling-point, is suddenly cooled as by pouring into cold water. It is

plastic and elastic, but becomes brittle on standing as it changes into crystals of the first form.

4. *Milk of Sulphur.*—When a strong acid is added to a polysulphid the sulphur is precipitated in a white and very finely divided form. This is sometimes used as a medicine. These last two forms are not distinct allotropic modifications.

Sulphur is used for the manufacture of sulphuric acid, for gunpowder, for vulcanizing rubber, and in the preparation of various compounds.

Experiment 40.—Heat sulphur in a test-tube to boiling and note carefully all the changes. When boiling hot pour out into cold water and examine.

Experiment 41.—Dissolve the sulphur that remains in the test-tube in carbon bisulphid (CS_2), filter into a beaker, and set away to crystallize.

Experiment 42.—Burn sulphur and note the odor of the gas formed. What is it?

Selenium

79. History.—This element was discovered by Berzelius in 1817 in a deposit from some sulphuric acid chambers. The name is derived from $\Sigma \varepsilon \lambda \acute{\eta} \nu \eta$, the moon.

80. Occurrence.—In small quantities along with sulphur in certain pyrites; also free. It is not found in many places and is far from being abundant.

81. Properties.—It is a solid, existing in two modifications—a red amorphous powder and dark crystals. Its specific gravity varies from 4.5 to 4.8 and it melts at 270°, boiling below a red heat, and giving off yellow vapors. In burning, it has a blue flame and the odor of decayed horse-radish. The chemical properties resemble those of sulphur, though selenium is less energetic.

Tellurium

SYMBOL Te. ATOMIC WEIGHT 127.49.

82. Occurrence.—Tellurium is found free. On this account it early attracted the attention of mineralogists and chemists but it was not recognized as a new element until the close of the last century. It is also found in a few rare compounds, notably with gold.

83. Properties.—It is a silvery-white solid with metallic lustre. Its specific gravity is 6.24 and its melting-point 452°, volatilizing at a white heat. It burns in the air with a bluish flame, and in the remaining chemical properties resembles sulphur and selenium.

TABLE OF THE PROPERTIES OF GROUP VI, NEGATIVE ELEMENTS.

Properties.	Oxygen.	Sulphur.	Selenium.	Tellurium.
Atomic weight····	16	32.07	79.02	127.49
Physical state·····	gas	solid	solid	solid
Color············	none	yellow	gray	silvery lustre
Specific gravity ··	0.8737	2.07	4.8	6.24
Melting-point ···· ······		115°	270°	452°
Boiling-point·····	—184.7°	440°	red heat	white heat

GROUP V

N 14.04
|
P 31.02
51.38 V   As 75.01
| |
93.73 Cb   Sb 120.43
| |
182.84 Ta   Bi 208.11

As in the case of the preceding groups, Series I will be omitted. The elements of this group have a valence of three toward hydrogen (bismuth forms no compound with hydrogen), and a valence of three or five towards oxygen. These elements show a strong negative character

which diminishes until the one with highest atomic weight is rather positive than negative.

Nitrogen

SYMBOL N.   ATOMIC WEIGHT 14.04.   GROUP ELEMENT.

84. History.—For a long time it has been known that part of the air could not support respiration nor combustion. In the latter part of the last century this was separated and purified. It was known as "mephitic" or "phlogisticated air." Lavoisier called it azote (from α privative and $\zeta\omega\acute{\eta}$ life). Chaptal gave it the name nitrogen as the former or generator of nitre.

85. Occurrence.—It is found free in the atmosphere of which it forms about four-fifths by volume and a little more than three-fourths by weight. Further it occurs combined with oxygen in nitric acid and its derivatives and with hydrogen in ammonia and the ammonium compounds. It is also an invariable constituent of protoplasm and is in many other vegetable and animal substances.

86. Preparation.—Nitrogen may be most easily prepared from the atmosphere by the removal of oxygen. This may be accomplished by burning phosphorus in an enclosed volume of air under a bell jar. This nitrogen is impure from the presence of small quantities of oxygen and also of the recently discovered element argon.

A purer nitrogen may be obtained by passing purified air over certain heated metals, as copper. Pure nitrogen is also obtained by heating ammonium nitrite.

$$NH_4NO_2 = 2H_2O + N_2.$$
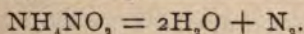
87. Properties.—Nitrogen is a colorless, odorless, transparent gas. It is a little lighter than air and can

be condensed to a liquid only by pressure at very low temperatures. It is less soluble in water than oxygen and is neither combustible nor a supporter of combustion. It is characterized by its inertness, combining with no element except lithium at ordinary temperatures and with very few when heated. Indirectly it can be made to combine with many of the elementary bodies, giving some very important compounds as ammonia and nitric acid and some remarkable ones as the explosives. The facts that most of the explosives are nitrogen compounds and that decay usually starts in compounds of nitrogen, show how easily it is separated from the other elements. It is not a poisonous element and indeed has no effect upon respiration. Its office in the atmosphere seems to be merely that of a diluent for the oxygen.

Experiment 43.—In a wide glass dish, half filled with water, float a porcelain crucible containing a small piece of phosphorus. Over the crucible place a stoppered bell jar. Ignite the phosphorus by touching with a hot wire and immediately close the bell jar with the stopper. After the oxygen of the air has been burned out and the fumes of the phosphorus pentoxid have subsided, fill the outer dish with water to the level of that in the bell jar, and test the nitrogen as to its combustibility and power of supporting combustion. By carefully noting the original volume of air and that of the residual nitrogen, the amount of nitrogen in the air can be determined. The amount of nitrogen in the air may also be determined by using a barometer tube inverted over water, removing the oxygen by inserting in the tube a piece of white phosphorus attached to a wire and allowing it to stand until the water ceases to rise in the tube.

The Atmosphere

Having studied the two chief components of the atmosphere, it is well to take up next the study of the atmosphere itself. By atmosphere is meant the gaseous envelope surrounding the earth. It extends to an indefi-

nite height above the earth, and presses at sea-level upon the earth with a pressure of about one kilo (2.0333 pounds) to the square centimeter, or nearly fifteen pounds to the square inch, equal to a column of mercury 760 mm. high. At 0° and a pressure of 760 mm., a liter of air weighs 1.293 grams. Its density compared with hydrogen is 14.37.

88. Composition.—The atmosphere consists chiefly of a mixture (not compound) of nitrogen and oxygen, the percentage of oxygen being 21 per cent. by volume and 23 per cent. by weight. It is important to prove that the air is a mixture. The fact that the proportions between the elements are very nearly constant would lead one to think that the air was a compound but on examination it will be seen that the quantities of oxygen and nitrogen do not present any simple relation to the atomic weights of these elements and moreover the proportions do vary slightly. Again on mixing the two elements in the proportion to form air there is no contraction of volume nor evolution of heat such as is always observed when chemical union takes place. And lastly when air is dissolved in water more oxygen is dissolved than nitrogen and so the proportion between the two elements is decidedly changed. This does not take place upon the solution of a compound.

The composition of the atmosphere may be determined volumetrically by means of an absorption cylinder in which a measured volume of air is subjected to the action of phosphorus or some other agent which will remove the oxygen and so permit the nitrogen to be measured. Or a eudiometer is used in which a known volume of air is mixed with a known amount of hydrogen and the mixture exploded by the electric spark.

Thus the oxygen can be determined and the nitrogen measured.

Gravimetrically, the composition of the air is usually determined by passing it over heated copper. The increase in weight of the copper corresponds to the amount of oxygen and the residual nitrogen can be weighed.

In addition to the oxygen and nitrogen in the air there are certain other constituents present in constant or in variable quantities.

89. Argon (density 19.9).—This is the largest in amount of these lesser ingredients of the air though its presence remained unknown until the year 1894. There is somewhat less than one per cent. of it in the atmosphere. It is characterized by an inertness greatly exceeding that of nitrogen, and it forms no known compound. Its function in the atmosphere is unknown. In fact very little is understood as yet about this most remarkable element.

90. Water.—The atmosphere takes up a large amount of water, the amount varying with the temperature. When the air has all the moisture it can hold it is said to be saturated. At ordinary temperatures a saturated atmosphere contains about 0.27 per cent. of water; at 0° it can hold but 0.04 per cent. When the atmosphere is cooled, this water is precipitated from the air as rain, snow, hail, etc. This moisture is condensed from the air by solids and porous substances like charcoal and the soil. It is also deposited in a visible film or as dew upon objects cooled below the temperature at which it would be saturated with the water present in it.

91. Carbon Dioxid.—This is present in the atmosphere to the extent, on the average, of 3 parts in

10,000. This amount varies slightly in different localities and at different times. Where processes of combustion are active, as in crowded rooms, the amount may far exceed this. Several agencies are continually adding carbon dioxid to the air. These are combustion, respiration of animals, and decay of organic matter. At the same time several agencies remove it from the air. It is consumed by plants, washed out by rains, and taken up by the oxids and hydroxids of the more positive elements, especially lime and magnesia. Much of the calcium carbonate formed is utilized by coral insects and shell-fish.

Other constituents of the atmosphere present in lesser and varying amounts are ammonia, ozone, hydrogen dioxid, volatile organic matter, and dust (including disease germs and other micro-organisms).

Phosphorus

SYMBOL P. ATOMIC WEIGHT 31.02. TYPE ELEMENT.

92. History.—This element was discovered in the seventeenth century, several alchemists laying claim to the discovery. It was first prepared from urine which contains several phosphates. It was prepared with much difficulty and was regarded as one of the most remarkable and interesting of bodies. As such it was exhibited at some of the courts of Europe.

93. Occurrence.—Owing to its strong affinity, especially for oxygen, phosphorus never occurs free. It occurs chiefly in the form of phosphates, which are compounds of phosphorus, oxygen, and some positive element. These are found in small amounts in rocks and soils from which it is taken up by plants and animals. Sometimes large deposits of these phosphates are found, as in

South Carolina, Florida, Spain, and other places. The mineral matter of bones is more than three-fourths calcium phosphate.

94. Preparation.—Bones on being charred give bone-black or "animal charcoal." This is first used in sugar refining and after it is spent it is calcined, leaving chiefly calcium phosphate. For a very long time phosphorus has been prepared from this compound. The first step is to treat this with sulphuric acid giving calcium sulphate and hydrogen calcium phosphate.

$$Ca_3(PO_4)_2 + 2H_2SO_4 = H_4Ca(PO_4)_2 + 2CaSO_4.$$
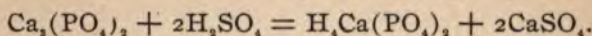
The calcium sulphate is allowed to settle and the solution of $H_2Ca(PO_4)_2$ is decanted and evaporated to a sirupy consistence. This is mixed with powdered charcoal, made into balls, which are thoroughly dried and then distilled in tubular retorts. The changes which take place are as follows:

$$H_4Ca(PO_4)_2 = 2H_2O + Ca(PO_3)_2.$$
$$2Ca(PO_3)_2 + 5C = + 5CO + Ca_2P_2O_7 + 2P.$$
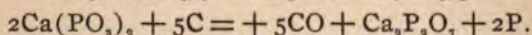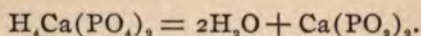
Only one-half of the phosphorus is obtained, the other half being in the form of calcium pyrophosphate, $Ca_2P_2O_7$. By mixing sand with the charcoal all of the phosphorus may be obtained. The phosphorus is distilled over into water and then, while melted under warm water, is strained through chamois skin and cast in cylindrical molds.

Phosphorus is largely made at present by the application of the high heat of the electric furnace to a mixture of calcium phosphate and charcoal. The phosphorus can be directly distilled off by this method.

95. Properties.—Phosphorus is a crystalline solid

existing in two or more allotropic states. The two most important are yellow or ordinary phosphorus and the red or " amorphous" phosphorus, as it has been called for a long time, though it has been recently shown to be minutely crystalline.

1. *Yellow Phosphorus.*—A pale, amber-colored, transparent, wax-like solid. It is brittle at low temperatures but cuts like wax at ordinary temperatures, melts at 44.3°, and boils at 290°. This is very slightly dissolved by hot water, is much more soluble in certain oils as turpentine, but its best solvent is carbon bisulphid. In a finely divided form, or as vapor, it is very poisonous. It unites readily with oxygen, burning to white oxids. It is very active chemically, showing strongly negative properties. Its kindling temperature with oxygen is 40° and it burns with great heat and light. At ordinary temperatures it oxidizes slowly with luminosity (phosphorescence) in the dark. It does not show this phosphorescence under great pressure nor in pure oxygen unless the pressure is reduced to about 150 mm. Because of the ease with which it oxidizes it must be preserved under water.

2. *Red Phosphorus.*—This is prepared by heating yellow phosphorus, with exclusion of oxygen, to 300°. It is also formed by the prolonged exposure of yellow phosphorus to the action of light. It forms a dark red, minutely crystalline mass which is insoluble in carbon bisulphid and alters very slowly in the air so that it need not be kept under water. It is not phosphorescent, nor poisonous, and is heavier than the first variety (specific gravity of yellow 1.83, of red 2.14). It does not ignite but at 260° it vaporizes and changes into the first form and will then burn.

Phosphorus is chiefly used for the manufacture of matches. For this purpose the red phosphorus is to be preferred because it is less poisonous and less inflammable. It is also used in making certain organic compounds, for vermin pastes, etc.

Experiment 44.—Compare white and red phosphorus as to inflammability by placing a small portion of each on a porcelain crucible cover and touching with a warmed wire.

Experiment 45.—Compare as to fusibility by placing a little of each in a test-tube containing water and warming. Use only small bits of white phosphorus (half the size of a pea) and *keep it under water while cutting!*

Experiment 46.—Dissolve a small piece of white phosphorus in 2 cc. carbon bisulphid. *Keep away from the flame!* When dissolved, pour it out on a piece of filter-paper and lay on the desk away from anything combustible. The carbon bisulphid rapidly evaporates, leaving a thin coating of phosphorus, which oxidizing very quickly raises the temperature above the ignition-point, and the phosphorus ignites. If carried out in the dark, the phosphorescence can be seen prior to the ignition.

Arsenic

SYMBOL As. ATOMIC WEIGHT 75.01.

96. Occurrence.—Arsenic, which has been known for a long time and was recognized as having metal-like properties by the alchemists, is found in the free state. It is however more abundantly found in combination with sulphur, and with the metals, especially iron and nickel. Two of its compounds with sulphur were known by the ancients and used as pigments.

97. Preparation.—It is obtained by roasting (heating in the air) any ore of arsenic, thus forming the oxid, As_2O_3, which is then reduced by heating with carbon.

$$As_2O_3 + 3C = 3CO + As_2.$$
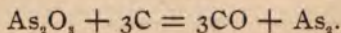
98. Properties.—Arsenic exists in two modifications (1) amorphous arsenic, a black, brittle solid, (sp. gr. 4.71,) and (2) crystallized arsenic, a steel-gray solid of brilliant metallic lustre with a specific gravity of 5.7.

Arsenic sublimes at 180° but can be melted only under pressure. It burns in the air with a blue flame to As_2O_3, giving off a garlic-like odor. It is insoluble in water and the ordinary solvents. Both varieties of arsenic may be obtained by subliming the element in a closed tube.

Chemically, arsenic is weakly negative. It combines with some of the positive elements forming arsenids. It also combines with the more negative elements, as chlorin and oxygen.

Experiment 47.—Place a little arsenious oxid (As_2O_3) in a closed tube (Fig. 11), and above it dry powdered charcoal. Heat the tube first opposite the charcoal and gradually extend the heat to the arsenious oxid. Note the arsenic "mirror" formed.

Fig. 11.

Experiment 48.—Sublime arsenic in a closed tube and note the two modifications formed.

Experiment 49.—Burn a very small piece of arsenic on charcoal before the blowpipe. Note the white fumes (what are they?), the blue color imparted to the flame, and the garlic odor.

Antimony

SYMBOL Sb. ATOMIC WEIGHT 120.43.

99. History.—Basil Valentine, about the end of the fifteenth century, first described the preparation of metallic antimony but not as a new discovery. Certain of its compounds were known in very early times and used as pigments. Pliny used the name *stibium* for

it and the symbol of the element comes from this word. The native sulphid or stibnite was called in Hebrew and Arabic '' Kohl'' and this word passed as '' alcool'' or '' alkohol'' into other languages. In the middle ages it meant any fine powder and later the spirits of wine.

100. Occurrence.—Antimony is found in compounds similar to those of arsenic and very often along with that element. It occurs free, and with sulphur in stibnite, Sb_2S_3. It is not so widely distributed nor as abundant as arsenic.

101. Preparation.—It may be obtained by heating the ore with scrap iron or by a method similar to that described for arsenic.

$$Sb_2S_3 + 3Fe = 3FeS + 2\ Sb.$$
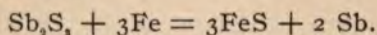
102. Properties.—It is a hard, brittle, steel-gray solid with a brilliant metallic lustre, crystalline and with a specific gravity of 6.7. It melts at 432°, volatilizes at a red heat, oxidizes readily in the air burning with a blue flame to Sb_2O_3, but it takes a higher temperature to kindle it than arsenic. With the positive elements it forms alloys or indefinite compounds. With the negative elements it combines readily. Hence it would rather be classed among the positive elements. Its chief use is in alloys, as in the alloy with lead in type metal.

Experiment 50.—Heat a small piece of antimony on charcoal before the blowpipe. Note the white fumes and the sublimate on the charcoal. What is it?

Bismuth

SYMBOL Bi. ATOMIC WEIGHT 208.11.

103. History.—Metallic bismuth was first described by Basil Valentine. Its discovery, like that of antimony, probably dates from an earlier period.

104. Occurrence.—It is chiefly found free. It is not widely distributed nor abundant. It may be obtained by melting it away from the veinstone or rocky material with which it is found.

105. Properties.—It is a reddish-white solid with metallic lustre, crystalline and brittle, though it possesses a slight degree of malleability. It is quite heavy, having a specific gravity of 9.5, melts at 264°, and is volatile at a red heat. It does not burn easily, but when heated to its kindling temperature in the air burns to Bi_2O_3. Bismuth forms alloys as antimony does and possesses electropositive characteristics, combining chiefly with negative elements.

Experiment 51.—Heat a piece of bismuth on charcoal before the blowpipe. Note the fumes and sublimate. How do they differ from those of arsenic and antimony? What are they? How does bismuth compare with antimony in fusibility?

106. Characteristics of the Group.—In this group, attention is to be especially drawn to the increase of electropositive characteristics with increasing atomic weight, nitrogen and phosphorus being strongly negative while antimony and bismuth are positive. All other properties also are seen to be graded in accordance with the atomic weight.

TABLE OF THE PROPERTIES OF GROUP V

Properties.	Nitrogen.	Phosphorus	Arsenic.	Antimony.	Bismuth.
Atomic weight	14.04	31.02	75.01	120.43	208.11
Physical state	gas	waxy solid	solid	solid	solid
Color	none	amber (red)	metallic lustre	metallic lustre	metallic lustre
Specific gravity	0.8660	1.83–2.14	4.7–5.7	6.7	9.5
Melting-point	.....	44.3°	......	432°	264°
Boiling-point	—193°	290°	......	....	....

GROUP IV

C 12.00
|
Si 28.40

48.15 Ti   Ge 72.48
| |
90.4 Zr   Sn 119.05
| |
139.35 Ce   Pb 206.92
|
232.63 Th

The elements of this group are all quadrivalent. Tin
and lead are also bivalent in most of their ordinary com-
pounds. Carbon and silicon are very abundant, tin and
lead are fairly so, while the others come under the head
of the rare elements, though titanium is very widely dis-
tributed. Carbon is the characteristic element of the
vegetable and animal kingdom ; silicon plays a similar
part in the mineral kingdom, being the characteristic
element of most rocks.

Carbon

SYMBOL, C.   ATOMIC WEIGHT 12.00.   GROUP ELEMENT.

107. Occurrence.—As carbon occurs very widely free
and has been recognized and used from the very earliest
times, its history of course cannot be traced. Free
carbon is found in three forms. These are the allotropic
modifications of the element.

I. *Diamond* is pure crystallized carbon. It was found
in earlier times in India, later on in Brazil, and now it is
obtained chiefly from South Africa. The diamond is also
found occasionally in almost every part of the world.
There are many theories as to how it was originally
formed but none are fully accepted. It may be artifi-
cially formed by crystallization under great pressure,

by dissolving in molten iron and allowing it to crystallize as the iron cools. These crystals are very small. The diamond has a specific gravity of about 3.5. It crystallizes in the regular system and is the hardest substance in nature. It can only be polished by means of other diamonds. Its action upon light is most noteworthy as it has very high dispersive and refractive powers. It is changed into the second form by very high heat or by the passage of electricity through it and it can be made to burn in oxygen and with greater difficulty in air. Its great lustre and brilliancy make it valuable as an ornament. Its hardness makes it useful for cutting and boring, as in the diamond drill.

II. *Graphite.*—This is also a crystallized variety of carbon, but the crystals are rhombic prisms instead of octahedra as in the case of the diamond. It is opaque, black, and very soft. It is found in many localities in primitive rocks. It is artificially formed when melted iron, which has absorbed a good deal of carbon, cools. It has a specific gravity of about 2.5 and can be burnt in oxygen. It is used as a lubricant, as a polish, and in the making of lead pencils and crucibles.

III. *Amorphous Carbon.*—To this class belong all the uncrystallized black varieties of carbon with an average specific gravity of 1.5. They differ from one another in the amount and nature of the foreign matter which they contain and in their compactness, some of them being noted for their porosity. The various forms of coal, coke, charcoal, soot, lampblack, etc., come under this heading. Some of the chief varieties are :

1. Anthracite or hard coal. This is the purest form of natural coal, and contains little or no volatile matter and little ash.

2. Bituminous or soft coal.   This contains more volatile matter than anthracite.

3. Cannel (" candle") coal containing much volatile matter and much ash.

These natural coals have been formed from the vegetable matter of the carboniferous (chiefly) period under the influence of pressure and heat.   They are found wherever carboniferous rocks are exposed, chiefly in this country along the Appalachian system, the soft coal being on the western side and the hard on the eastern.

4. Brown coal or lignite (one variety *jet*).   This is coal of later (tertiary) period and is less pure and compact.

5. Peat.   This is coal in the early stage of formation, of the present period.

6. Charcoal.   This is prepared from wood by heat without exposure to the air ; also from bones and blood— animal charcoal, bone-black.   Wood charcoal is the purest common form of amorphous carbon.

7. Coke.   This is obtained from soft coal by heating without access of air.

8. Gas carbon.   This is very compact carbon from gas retorts.

9. Soot or lampblack.   A quite pure carbon from the imperfect combustion of oils and resins.

All varieties of carbon are insoluble in everything except certain molten metals and are infusible and non-volatile at the highest temperatures we can reach, except those obtained by the aid of electricity.

Carbon further occurs very largely in the combined state :

1. With hydrogen and oxygen in all plants and animals and organic substances in general.

2. With oxygen in carbon dioxid in the atmosphere. The amount of this has been estimated at four billion tons.

3. With oxygen and some positive element in carbonates; limestone or calcium carbonate is particularly abundant.

Experiment 52.—Heat a few bits of soft coal in a closed tube. Notice what is evolved and what is left in the tube.

Experiment 53.—Heat similarly a few bits of anthracite coal. Does any change take place?

Experiment 54.—Heat similarly a few bits of wood. Compare with the above.

Experiment 55.—Examine graphite; heat on platinum foil; compare with the action of coal or charcoal under similar circumstances.

108. Properties.—The physical properties have been already given under the head of the allotropic forms. Chemically, carbon is a negative element. At ordinary temperatures, it shows but slight affinity for any other element. At high temperatures, its affinity for oxygen is very great and any of the above forms will burn to carbon dioxid. As this combustion gives forth great heat it is our chief fuel and is used in immense quantities for metallurgical purposes, both as a source of heat and for reducing purposes. Many of the ores of the metals are oxids or can be transformed into oxids. On heating these with carbon, the oxygen is removed as carbon monoxid.

$$ZnO + C = Zn + CO.$$
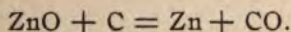
Carbon unites at high temperatures with sulphur giving carbon bisulphid. With many positive elements as aluminum, calcium, etc., it unites at the temperature of the electric furnace giving compounds called carbids, some of which have found industrial application.

Charcoal, on account of its porosity, has the power of condensing large quantities of gases and water-vapor. Animal charcoal made from bones is used to remove impurities, colors, etc., from solutions, as in the sugar refineries.

Experiment 56.—Burn a piece of charcoal in a bottle; pour in a little lime-water and shake it around the sides of the bottle. What is formed by the combustion of the carbon, and what causes the precipitate in the lime-water?

Experiment 57.—To a hot solution of litmus in a test-tube add some animal charcoal and shake a few moments. Pour through a filter and compare the filtrate with the original solution.

Experiment 58.—Mix arsenious oxid (As_2O_3) (white arsenic) with about half its weight of charcoal (both finely pulverized); put in the bulb of a closed tube and heat. What sublimes on the sides of the tube?

Experiment 59.—Mix litharge (PbO) with one-tenth its weight of finely powdered charcoal. Heat in a test-tube fitted with a small delivery-tube dipping below the surface of lime-water in another test-tube. After the reaction is over, examine the residue in the tube by rubbing with water in a mortar, and washing out the unchanged charcoal. What is the residue? What gas was given off?

Silicon

SYMBOL Si. ATOMIC WEIGHT 28. TYPE ELEMENT.

109. Occurrence.—It is never found uncombined. In compounds it is very abundant and occupies in the mineral or inorganic world much the same place as is occupied by carbon in the organic.

It is found combined with oxygen in silica (SiO_2) which exists in many forms and in great abundance, as quartz, flint, agate, sand, sandstone, etc. It may also be combined with oxygen and some positive element. These compounds are known as silicates and constitute the larger portion of the crystalline rocks. Silicon is thus,

next to oxygen, the most abundant element upon the earth's surface, constituting about one-fourth of it by weight.

110. Preparation.—*a*. By the action of metallic sodium on sodium silico-fluorid at a high temperature.

$$Na_2SiF_6 + 4Na = 6NaF + Si.$$
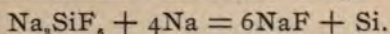
b. Or by heating silica with magnesium.

$$SiO_2 + 2Mg = 2MgO + Si.$$
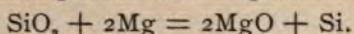
111. Properties.—Obtained in this way, silicon is a dark amorphous powder, burning, when heated in the air, to silica. It is soluble in hydrofluoric acid but not in other acids. It dissolves in melted zinc or aluminum, from which it crystallizes in brilliant octahedra, resembling the diamond and having a specific gravity of 2.49. It will not dissolve in any acid and cannot be burned in the air or oxygen.

Amorphous silicon is analogous to coal and there is some evidence to show that silicon exists in a third form analogous to graphite.

Silicon combines with the positive elements at the temperature of the electric furnace forming silicids.

The four elements of the positive series, Group IV, belong to the class of rare elements and will be considered together as they require very little separate discussion.

POSITIVE SERIES OF GROUP IV

112. Titanium (Ti, 48.15) occurs mainly in the same way as the type element silicon; that is, as the oxid, TiO_2, and also along with silica. It is quite often met with in iron ores. In minute amounts it is very widely disseminated in almost all soils and probably in most rock masses. It is also found in small amounts in plants and animals. **Zirconium** (Zr, 90.4) is found mainly com-

bined with silica in the mineral zircon, also as the oxid, and in a few other minerals. **Cerium** (Ce, 139.35) and **thorium** (Th, 232.6) also occur combined with silica. The latter is especially rare.

113. Preparation.—Titanium, zirconium, and thorium are obtained by a method analogous to that by which silicon is obtained; namely, the reduction of K_2TiF_6, K_2ZrF_6, or K_2ThF_6 by means of metallic sodium. Cerium is obtained by the reduction of the chlorid with metallic sodium.

114. Properties.—These elements are dark, with metallic lustre, burn in oxygen or the air to the dioxid, and are not easily acted upon by acids. In their chemical nature (with the exception of cerium) they show considerable analogy to silicon. The difference exhibited by cerium suggests the thought that when this element has been more thoroughly studied it may prove to be out of place in this group.

NEGATIVE SERIES OF GROUP IV

When we come to the second or negative series of this group, the first element, **germanium** (Ge, 72.48), is to be classed among the rarest of the elements, occurring in a few very rare minerals. The element is prepared in a manner similar to the preparation of silicon and exhibits some similarity of properties. A peculiar interest attaches to germanium as its properties and those of its compounds correspond very closely to those of an element predicted by Mendeléeff long before the discovery of germanium.

Tin

SYMBOL Sn. ATOMIC WEIGHT 119.05.

115. History.—This metal was known in very early

times. It was probably brought from the British Isles by the Phoenicians and was certainly known to the Romans at the beginning of our era. Tin was originally called *plumbum candidum*, but the word *stannum*, which first seems to have signified a mixture of metals, gradually became identified with tin and from it the symbol is derived.

116. Occurrence.—Tin is found chiefly as the dioxid, SnO_2. This is the common mode of occurrence for the elements of this group. This tin dioxid is called tinstone and is known mineralogically as cassiterite. It is not very widely distributed. The early supplies of tin came from the mines in Cornwall. At present it is obtained from Banca, Biliton, Australia, etc. Tin was not used in the pure state in early times but alloyed with copper as bronze.

117. Preparation.—Tin is obtained practically by heating the dioxid with carbon

$$SnO_2 + C_2 = Sn + 2CO.$$
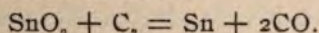
118. Properties.—It is a silvery white solid with metallic lustre, soft and malleable, capable of being hammered out into thin sheets (tin foil). Just below its melting-point it is brittle and may be pulverized. It melts at 228° and boils at a white heat. Its specific gravity is 7.2. It does not tarnish or rust at ordinary temperatures but it burns when highly heated in the air, forming stannic oxid, SnO_2. Tin unites directly with the more negative elements thus showing a positive nature. It dissolves in hydrochloric acid and sulphuric acid but is oxidized by nitric acid to a hydroxid which exhibits acid properties. It forms two classes of compounds, *stannous* in which it is bivalent, and *stannic* in which it is quadrivalent.

Tin is used to some extent in the pure state as block tin, but more commonly in alloys and as a coating for other metals, as iron (giving tin plate), and copper. Its most important alloys are bronze (tin and copper) and solder (tin and lead).

Experiment 60.—Reduce stannic oxid (SnO_2) on charcoal before the blowpipe, using potassium cyanid (KCN) as a flux. Examine the residue by rubbing with water in a mortar.

Experiment 61.—Dissolve a small piece of tin foil in strong hydrochloric acid, and add the solution obtained to a few drops of mercuric chlorid ($HgCl_2$). The mercury salt is reduced by stannous chlorid ($SnCl_2$) to metallic mercury, a gray powder, the stannous chlorid becoming changed to stannic chlorid ($SnCl_4$).

Experiment 62.—Add concentrated nitric acid to a piece of tin foil. What is formed?

Lead

SYMBOL Pb. ATOMIC WEIGHT 206.92.

119. History.—Lead was one of the earliest known metals and is mentioned in the Bible and other very ancient writings. It was not always clearly distinguished from tin. The Roman writer, Pliny, gave it the name *plumbum nigrum* to distinguish it from *plumbum candidum*, or tin.

120. Occurrence.—It is chiefly found combined with sulphur. This ore is called galena and is found in considerable quantities in many places.

121. Preparation.—1. The galena (sulphid) may be heated with iron which has more affinity for the sulphur than has lead.

$$PbS + Fe = FeS + Pb.$$
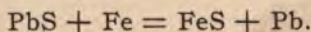
2. More commonly, the sulphid is partially roasted giving a mixture of lead sulphid, lead oxid, and lead

sulphate, which is reduced by excluding further access of air and raising the temperature.

$PbS + 2PbO = SO_2 + 3Pb$ and $PbS + PbSO_4 = 2SO_2 + 2Pb$.
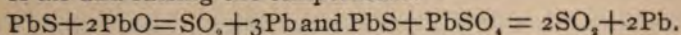
This roasting is carried out in a reverberatory furnace. One form of this class of furnace is seen in Fig. 12. The grate is shown at A ; the fire box at B ; the fire
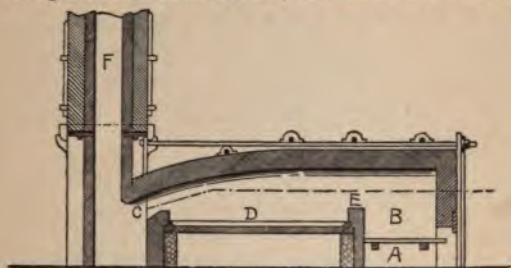
Fig. 12.

bridge at E ; the hearth upon which the ore is placed at D. The arched roof above deflects the flame and heat upon the ore below; C is the flue and F the chimney. As the hot air passes over the ore in this furnace some of the sulphur is oxidized and burns to sulphur dioxid which passes up the chimney while some of the sulphid is oxidized to sulphate. From time to time the ore is turned over by a workman, who inserts his paddle or '' slice'' through a side door, and exposes a fresh surface to the action of the hot air.

122. Properties.—Lead is a bluish white solid of metallic lustre, very soft, quite malleable, but lacking in tensile strength. It melts at about 335° and has a specific gravity of 11.25. It tarnishes readily in the air, owing to oxidation, but this action penetrates into the mass very slowly. At higher temperatures it oxidizes rapidly forming lead oxid (PbO). It unites with sulphur readily at a high temperature but not very readily with other negative elements. It is insoluble in dilute hydro-

chloric and sulphuric acids but is readily dissolved by nitric acid. In its ordinary salts it is bivalent. Lately a class of salts have been discovered in which it is quadrivalent. It is used for lead pipe, sheet lead, and many alloys. The use of lead pipe in connection with drinking water is dangerous, as the water and air slowly act upon the lead and some of it is dissolved. As the lead compounds formed are very poisonous, and as lead acts as a cumulative poison (collecting in the system until serious poisonous effects are felt), such use of lead pipe should be avoided.

Experiment 63.—Heat some litharge (PbO) on charcoal before the blowpipe. Note the difference in the appearance of the lead in the oxidizing and in the reducing flame.

Experiment 64.—Test the action of lead on dilute hydrochloric acid, nitric acid, and sulphuric acid. What difference is noted? How can you tell whether any lead is dissolved?

TABLE OF THE PROPERTIES OF GROUP IV

	Element.	At. wt.	Sp. gr.	M. P.
Positive series	C	12.01	1.5-3.5	(2500°)
	Si	28.4	2.49	(1200°)
	Ti	48.15	5.1	(2500°)
	Zr	90.4	4.1	(1500°)
	Ce	139.35	6.6	(700°)
	Th	232.6	11.1	....
Negative series	Ge	72.48	5.47	900°
	Sn	119.05	7.2	228°
	Pb	206.92	11.25	335°

GROUP III

B 10.95
|
Al 27.11

44.12 Sc   Ga 69.91
| |
89.02 Y   In 113.85
| |
138.64 La   Tl 204.15

These elements all exhibit a valence of three toward oxygen and form no well-characterized compounds with hydrogen. Boron and aluminum are the only ones which are not rare elements and which have important compounds.

Boron

SYMBOL B. ATOMIC WEIGHT 10.95. GROUP ELEMENT.

123. Occurrence.—It is never found free but always combined with oxygen and hydrogen as boracic or boric acid ; and in compounds of this acid with the positive elements. Its chief compound is borax, $Na_2B_4O_7$, which occurs in a number of localities and in considerable amounts.

124. Preparation and Properties.—Boron may be prepared by reducing boron trioxid with sodium.

$$B_2O_3 + 6Na = 3Na_2O + B_2.$$
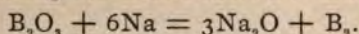
It is a brown amorphous powder which may be dissolved in melted aluminum from which it crystallizes, on cooling, in dark brilliant crystals, resembling those of the diamond in lustre and hardness. It can be melted only by means of electricity. The crystallized variety has a specific gravity of about 2.6 and burns with even greater difficulty than the diamond. Boron can be made to combine directly with nitrogen, a property not shown by many elements. It is the only element of the third group which possesses negative properties, thus bridging over from the third to the fourth group. Like carbon and silicon it combines with positive elements in the electric furnace, giving borids.

Aluminum

SYMBOL Al. ATOMIC WEIGHT 27.11. TYPE ELEMENT.

125. History.—The difficulty of separating this ele-

ment, from its compounds which occur in nature, prevented its early discovery. In the first part of this century it was recognized that clay contained a new element but all efforts at isolating it were futile. It was not until 1827 that Wöhler succeeded in separating and examining the element. Its cheap separation still presents many difficulties to the metallurgist.

126. Occurrence.—It is never found free. Its most abundant compound is clay in which it is united to oxygen and silicon. Along with other elements, as well as these two, it is found in many minerals, as feldspar, mica, etc. Combined with oxygen it constitutes corundum, known in the impure state as emery. It is also the chief constituent of the ruby, sapphire, and other precious stones. Cryolite, the double fluorid of sodium and aluminum, and bauxite, the hydrated oxid of aluminum, are the chief ores from which the element is obtained at present.

127. Preparation.—The method used until recently was the decomposition of the chlorid, or the double chlorid with sodium, by means of sodium.

$$AlCl_3.3NaCl + 3Na = 6NaCl + Al.$$
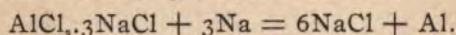
At present, it is prepared by the action of the electric current upon the oxid dissolved in cryolite which has been fused by the heat of the current.

128. Properties.—Aluminum is a white solid with silvery lustre, melting at about 700°. It has a specific gravity of 2.7 and this lightness is one of its most remarkable properties. It is moderately tenacious and very malleable, having about the softness of silver. Aluminum does not tarnish readily, not being acted upon when pure by oxygen at ordinary temperatures.

It is easily dissolved by hydrochloric acid and by alkalies. It is also acted upon by vegetable acids especially in the presence of salts. It has a strong affinity for oxygen at high temperatures and so is used to reduce oxids and set free other elements, which were combined with it. Until recently the high price of aluminum has precluded its general use. It is now, however, coming into use for many purposes where a light metal is of advantage, as instruments, ornaments, domestic utensils, military accoutrements, etc. It is also used in alloys, as with copper in aluminum bronze which possesses great strength, and in iron castings to promote molding qualities. Its uses will probably be extended in the future as it becomes cheaper but it can scarcely come up to some of the exaggerated expectations as to its usefulness.

Experiment 65.—Examine aluminum ; test it before the blow-pipe ; test its solubility in acids and in sodium hydroxid.

POSITIVE AND NEGATIVE SERIES OF GROUP III

The remaining elements of this group are quite rare and can be briefly considered together. **Scandium** is of interest because it was predicted by Mendeléeff and was afterwards discovered and found to have properties agreeing with those predicted for it. The same is true of **gallium.** The latter has been shown to be quite widely distributed, occurring in a number of ores and minerals but always in very minute quantities. **Yttrium** seems also to be widely distributed but in small amounts. Probably the most abundant of these is **thallium.** This element (Tl, 204.15) was discovered by Crookes by means of the spectroscope in the deposit in the flue of a pyrites burner. The spectroscope has been the chief instrument in discovering the rare elements of this group.

Metallic thallium closely resembles lead in its physical properties. It forms two classes of salts, thallous in which it is univalent, and thallic in which it is trivalent. Its name is derived from the green line in its spectrum by which it was discovered. All of these elements resemble aluminum in some respects but those of the first series are more nearly akin to it.

TABLE OF THE PROPERTIES OF GROUP III

	Element.	At. wt.	Sp. gr.	M. P.
Positive series.........	B	10.95	2.5	(1300°)
	Al	27.11	2.7	700°
	Sc	44.12	(2.5)	....
	Y	89.02	(3.4)	....
	La	138.64	....	....
Negative series.......	Ga	69.91	5.96	30°
	In	113.85	7.4	176°
	Tl	204.15	11.8	294°

GROUP II

Gl 9.08
|
Mg 24.28

40.07 Ca   Zn 65.41
| |
87.61 Sr   Cd 111.95
| |
137.43 Ba   Hg 200.00

The elements of the second group are all bivalent toward oxygen and form no distinctive compounds with hydrogen. All of these elements are strongly positive. All except glucinum are fairly abundant and several of them belong to the class of useful metals.

Glucinum

SYMBOL, Gl. ATOMIC WEIGHT 9.08. GROUP ELEMENT.

This element is also known as beryllium. Its occurrence as a silicate (beryl) and along with aluminum,

links it to the preceding group. It is prepared like aluminum by decomposing its chlorid by means of sodium. It dissolves readily in acids and much resembles magnesium. It has a specific gravity of 2.1 and does not decompose water even at a high temperature, nor does it in compact form readily oxidize when heated to a high temperature. In the finely divided state it takes fire when heated in the air and burns with great brilliancy.

Magnesium

SYMBOL Mg. ATOMIC WEIGHT 24.28. TYPE ELEMENT.

129. History.—It was the English chemist Black who first pointed out clearly the distinctions between the compounds of magnesium and those of calcium, particularly the carbonates. This was in the latter part of the last century; up to that time there had been much confusion as to the compounds of this element. It was through the labors of Davy that the element was isolated, and after a while the name magnesium was generally adopted for it.

130. Occurrence.—Magnesium is never found free but its compounds are widely distributed and abundant. It occurs as the carbonate, called magnesite; as a double carbonate with calcium, called dolomite, also called magnesian limestone; in silicates as meerschaum, talc, and soapstone; as the sulphate and as the chlorid in sea-water and salt deposits.

131. Preparation.—It may be obtained by the decomposition of the chlorid by means of metallic sodium. It may also be prepared electrolytically.

132. Properties.—Magnesium is a silvery white solid, malleable, and very light, having a specific gravity of 1.75.

It tarnishes in the air slowly at ordinary temperatures but, when the temperature is raised, it shows great affinity for oxygen, burning with a brilliant white light. This light is strong in what are called the chemical rays of the spectrum and, before the day of the electric light, was largely used for the taking of photographs. It is still used along with zinc for flash-lights. Owing to its strong affinity for oxygen it is used to reduce some of the oxids of the rare metals. At ordinary temperatures it does not decompose water but it does at the boiling-point. It dissolves readily in acids.

Experiment 66.—Test magnesium before the blowpipe and also as to its solubility in the acids, and in sodium hydroxid.

Calcium

SYMBOL Ca. ATOMIC WEIGHT 40.07.

The elements of this series were first separated from their oxids by Davy during the first decade of this century by means of the electric current.

133. Occurrence.—Calcium is found combined as the carbonate, limestone ; the sulphate, gypsum ; and the silicate. It is very abundant and widely distributed.

134. Preparation.—It may be prepared with difficulty by the decomposition of the chlorid by sodium or by electricity.

135. Properties.—It is a yellow, lustrous solid, oxidizing so readily that it must be kept under oil. It decomposes water at ordinary temperatures, with the evolution of hydrogen. It has a specific gravity of 1.6. When heated to redness in the air it burns with a very bright, orange-yellow flame.

Strontium

SYMBOL, Sr.   ATOMIC WEIGHT 87.61.

136. Occurrence and Properties.—The same compounds are found as in the case of calcium. The carbonate is known as strontianite, the sulphate as celestite. The silicate is not common. The preparation is like that of calcium. The properties are also similar. The specific gravity is 2.5 and the flame given on burning is red.

Barium

SYMBOL, Ba.   ATOMIC WEIGHT 137.43.

137. Occurrence and Properties.—This element also occurs as the carbonate or witherite and the sulphate or heavy spar; the silicate is rarer. The preparation and properties are similar to those of calcium and strontium. The specific gravity is 3.75.   It burns with a green flame.

Zinc

SYMBOL, Zn.   ATOMIC WEIGHT 65.41.   SERIES 2.

138. History.—Zinc ore was used for the making of brass, an alloy with copper, in very early times, but the free metal was not prepared and used until during the middle ages.

139. Occurrence.—It is chiefly found as the sulphid, called zinc blende, also as the carbonate, silicate, and oxid. It is fairly abundant and its ores generally contain a number of other metals.

140. Preparation.—The sulphid is first roasted ; that is, heated in the air with free access of oxygen. It is thus oxidized.

$$ZnS + 3O = ZnO + SO_2.$$
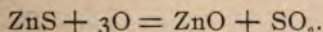
This oxid is then reduced by heating in retorts with

carbon. This is a very common operation in the reduction of metals from their ores.

$$ZnO + C = Zn + CO.$$
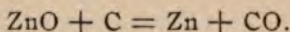
At the temperature to which the retort must be heated for this reaction, the zinc is a gas. It therefore escapes from the retort along with the carbon monoxid which is also a gas. As it is a very heavy gas special precautions have to be adopted to prevent its leaking from the retort. The process most commonly used is called the Belgian (see Fig. 13). A clay tube C, closed at one end,
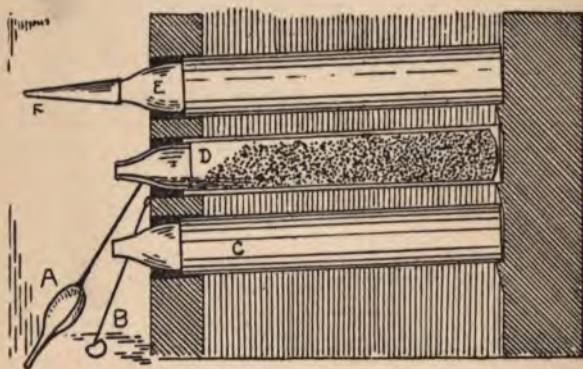
Fig. 13.

is used as the retort. This is placed in the furnace in an inclined position. The open end is connected with an adapter E which projects from the front of the furnace. The zinc vapor condenses in this adapter and is drawn out from time to time in a ladle A by means of a scraper B. F is made of sheet iron and is intended to condense any zinc which would otherwise escape when the retort gets very hot.

141. Properties.—It is a solid, with a bluish white color and metallic lustre, melting at 433° and boiling at 940°. Its specific gravity is 6.9. Its malleability varies with the temperature. At ordinary temperatures it is rather brittle, at 100°–150° it is decidedly malleable and can be rolled out into sheets, while at higher temperatures, below its melting-point, it is very brittle and can be pulverized. It tarnishes rapidly in moist air, but the tarnish forms an impervious coating and is hence superficial. At high temperatures it unites with oxygen readily, burning with a greenish white flame. It dissolves easily in acids and also in caustic alkalies, giving off hydrogen. Zinc is used as sheet zinc for roofing and other purposes, for galvanic batteries, for coating iron (galvanized iron) and in alloys.

Experiment 67.—Try to reduce zinc oxid before the blowpipe. Why can you not get the metal? Test the solubility of the metal in acids and in sodium hydroxid.

Cadmium
SYMBOL Cd. ATOMIC WEIGHT 111.95.

142. History.—This element was discovered in 1817 in some impure zinc carbonate. Its presence, which had not been recognized before, gave the carbonate a peculiar appearance, and its giving a yellow precipitate with hydrogen sulphid caused it to be suspected that the zinc carbonate contained arsenic. On examination the new element was discovered.

143. Occurrence.—It is found mainly with zinc blende in small amounts and also in the carbonate.

144. Preparation.—In the process of extracting zinc the first zinc which distils over contains any cadmium which may be present, and the cadmium may be separated from it.

145. Properties.—It is a solid with a white color and metallic lustre. It is fibrous and not crystalline like zinc and therefore can be bent, rolled, and hammered. It melts at 320° and boils at about 800°. Its specific gravity is 8.6. It is less easily soluble in dilute acids than zinc. It is mainly used in certain alloys which fuse at a low temperature.

Experiment 68.—Test cadmium before the blowpipe and also its solubility in acids.

Mercury

<center>SYMBOL Hg. ATOMIC WEIGHT 200.</center>

146. History and Occurrence.—As mercury is found free and can also be easily gotten from its ore, it has been known for a long time. The earliest mention of it dates back to 300 B. C. Not much of it is found free. It is chiefly found combined with sulphur, as cinnabar.

147. Preparation.—It can be prepared by simply burning or roasting the ore in the air.

$$HgS + O_2 = Hg + SO_2.$$
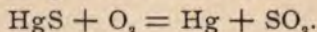
This mode of preparation is possible in the case of a few elements only, as they will usually combine with the oxygen under these circumstances.

148. Properties.—Mercury is the only positive element which is a liquid at ordinary temperatures. It is opaque and has a brilliant silvery lustre. It becomes solid at —39° and boils at 360°. It is very heavy, having a specific gravity of 13.59. When pure it is unaffected by the atmosphere at ordinary temperatures, but just below its boiling-point it is oxidized to the red oxid, HgO. Like most of the elements thus far considered it combines directly with chlorin. It is nearly insoluble in hydrochloric and cold sulphuric acid, but dissolves readily in

dilute nitric acid. It forms two classes of compounds, *mercuric* in which it is bivalent, and *mercurous* in which it is univalent. It dissolves many metals, forming amalgams (mercury alloys). It is used in barometers and thermometers, in the reflecting surface for mirrors, and for extracting silver and gold from their ores. The vapor of mercury is very poisonous as are also most of its compounds. This metal, in mass, is nearly insoluble in the animal secretions and so does not act poisonously, but when finely divided it is acted upon by them.

Experiment 69.—Heat mercuric sulphid (HgS) in an *open* tube. What passes off and what is obtained in the tube?

Experiment 70.—Mix a little mercuric sulphid with sodium carbonate and heat in a *closed* tube. What is obtained?

Experiment 71.—Add chlorin water to a minute drop of mercury. What takes place? Test a drop of mercury with hydrochloric acid; with sulphuric acid; and with nitric acid.

Experiment 72.—Test a mercurous nitrate ($HgNO_3$) solution with sodium hydroxid; with potassium iodid. Treat a mercuric compound (nitrate or chlorid) similarly. Write the equations for the reactions.

TABLE OF THE PROPERTIES OF GROUP II.

Elements.	At. wt.	Sp. gr.	M. P.
Gl	9.08	1.64	($900°$)
Mg	24.28	1.74	$500°$
Ca	40.07	1.6	$800°$
Sr	87.61	2.5	$600°$
Ba	137.41	3.75	....
Zn	65.41	7.2	$230°$
Cd	111.95	8.6	$320°$
Hg	200.00	13.59	$-39°$

GROUP I

Li 7.03
|
Na 23.05
/   \
39.11 K   Cu 63.60
| |
85.43 Rb   Ag 107.92
| |
132.89 Cs   Au 197.23
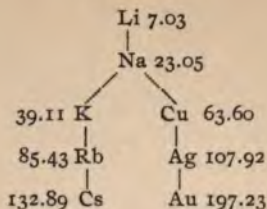
The elements of the first group resemble each other in having a valence of one, but copper is also bivalent and gold trivalent.   All are strongly positive elements. The first five of these elements resemble each other very closely and are known as the alkalies. Of these, lithium is comparatively rare and rubidium and cesium are very rare.   These five elements will be treated together.

Lithium, Li 7.03 ; **Sodium,** Na 23.05 ; **Potassium,** K 39.11 ; **Rubidium,** Rb 85.45 ; **Cesium,** Cs 132.89.

149. History.—For a long time the caustic alkalies, or alkaline hydroxids, were accepted as undecomposable. In 1807 Davy decomposed these by the electric current, obtaining the metals sodium and potassium.   Lithium was discovered in 1817 by Arfvedson. Rubidium (1861) and cesium (1860) were discovered by Bunsen by means of the spectroscope.

150. Occurrence.—Owing to their strong affinities the alkalies are never found free. Lithium is a constituent of a few silicates. It is also found in some soils, plants, and waters. It is thus widely distributed but is found only in small amounts.   Sodium is found in many silicates, also as sulphate, carbonate, nitrate, borate, etc., but its chief compound is the chlorid, NaCl (common salt), which is found in sea-water, in large deposits

(rock salt), and in small amounts along with a great number of other substances. It is necessary for animal life and is found in the ashes of seaweeds.

Potassium is found as a constituent of a number of silicates, such as mica, feldspar, etc. It also occurs as the nitrate, chlorid, sulphate, etc. It frequently accompanies sodium. It is necessary to plant life and was obtained chiefly from wood-ashes before the discovery of the Stassfurt salt beds in Germany. These beds furnish most of the potassium compounds at present. Rubidium and cesium are found widely distributed in traces accompanying sodium and potassium compounds.

151. Preparation.—The fused chlorids or hydroxids may be decomposed by a strong electric current. This is the original method by which the alkalies were obtained. The more usual method is to reduce the carbonate at a high temperature by means of carbon. This does not apply in the case of lithium but is used mainly for potassium.

$$K_2CO_3 + 2C = 2K + 3CO.$$
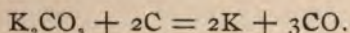
In the case of sodium the metal is best obtained by allowing fused sodium hydroxid to drop upon highly heated coke in a retort. The carbon unites with the oxygen and the sodium distils off.

$$2NaOH + C = H_2O + CO + 2Na.$$
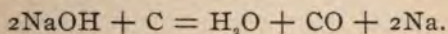
152. Properties.—These elements have a metallic appearance with bright lustre on freshly cut surfaces, are soft at ordinary temperatures, have low melting-points, and are lighter than water. Lithium is the lightest of all known solids. They are all characterized by an intensely strong affinity for oxygen. They decompose water at ordinary temperatures, forming a

hydroxid and evolving hydrogen. In the case of potassium (and sodium when the action is confined to one spot), the heat generated by the reaction is sufficient to ignite the hydrogen.

$$2Na + 2H_2O = 2NaOH + H_2.$$
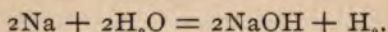
Exposed to the air these elements speedily oxidize. They should therefore be preserved under some substance, as benzene or kerosene, which contains no oxygen.

Lithium is peculiar in combining with nitrogen at ordinary temperatures to form a nitrid (Li_3N). The costliness of most of the alkalies prevents their being put to any practical use, with the exception of sodium which, on account of its strong affinity for chlorin and oxygen, is used to some extent as a reducing agent in the preparation of other elements, as aluminum, and is also added to the mercury used in the extraction of gold and silver.

Experiment 73.—Test the action of potassium and of sodium on water. Note the difference and explain.

Experiment 74.—Expose a freshly cut surface of sodium or potassium for a few moments to the air. What takes place?

Experiment 75.—Compare the color of the flame of salts of lithium, sodium, and potassium. Use a platinum wire. Examine the flame through blue glass.

NEGATIVE SERIES OF GROUP I

This includes the elements copper, silver, and gold. These elements exhibit many analogies and have many points of resemblance. In other respects they are quite dissimilar. All occur uncombined, gold almost exclusively so. They are very commonly found together. They were among the first known of the elements and are mentioned in the earliest historical writings.

Copper

SYMBOL Cu. ATOMIC WEIGHT 63.60.

153. Occurrence.—Native copper is found in large amounts in Michigan. Copper is also found as the oxid, carbonate, and as the sulphid. This last is very commonly combined with iron sulphid. Copper silicate is another one of the ores of copper.

154. Preparation.—Native copper needs only to be melted and refined. The oxids and carbonates are reduced with carbon. Copper glance, or the sulphid, is first partially roasted and the oxid thus formed made to react with the unchanged sulphid by heating with exclusion of air. If iron sulphid is present this must first be removed by partial roasting and fusing with sand.

$$Cu_2S + 2O_2 = 2CuO + SO_2.$$
$$Cu_2S + 2CuO = SO_2 + 4Cu.$$
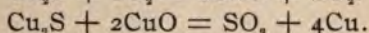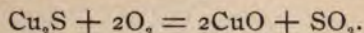
155. Properties.—Copper is the only red metal. It melts at 1090° and has a specific gravity of 8.8 It is very malleable and can be drawn out easily into wire. It is an excellent conductor of heat and electricity. It oxidizes very slightly in pure air or oxygen at ordinary temperatures. The moisture and carbon dioxid of the air will gradually corrode it. At higher temperatures it readily oxidizes. At a high temperature it burns with a green flame. Copper is easily dissolved by nitric acid but is slowly acted upon by hydrochloric and sulphuric acids at ordinary temperatures. Copper gives two classes of salts. In its cuprous compounds it may be considered univalent, in the cupric bivalent. It is a poisonous metal. Copper is used for boilers and cooking vessels on account of its conducting power for heat. It is used for electric wires, etc., on account of its con-

ducting powers for electricity. It is further used for coinage. The largest use of copper is in its alloys which are very important, copper forming more useful alloys than any other metal. Brass is an alloy of copper and zinc; bronze is an alloy of copper and tin; aluminum bronze has aluminum instead of tin; German silver contains copper, zinc, and nickel. The copper alloys are, in general, much harder than copper and can be cast and worked with a lathe or file. Copper cannot be easily cast.

Experiment 76.—Test the fusibility of copper before the blowpipe.

Experiment 77.—Test the solubility of copper in hydrochloric, in nitric, and in hot concentrated sulphuric acids.

Silver

SYMBOL Ag. ATOMIC WEIGHT 107.92.

156. Occurrence.—Silver is found free or native and also combined as the sulphid, the chlorid, and other rarer compounds. It very commonly accompanies lead in its ores.

157. Preparation.—The silver ores would be easy to treat metallurgically were it not for the small amount of silver usually contained in them. Mercury is often used to gather up the silver in the ore and then the mercury is driven off by heating ; or lead may be used to collect the silver and the lead removed by oxidation and cupellation. The first is called an amalgamation and the last a cupellation process. Silver chlorid may also be dissolved out of the ore by means of certain solvents, as a solution of potassium cyanid, and the silver then precipitated.

158. Properties.—This is a white and very lustrous

metal, melting at 1000° and having a specific gravity of
10.5 It is an excellent conductor of heat and electricity.
It is very malleable and can be drawn out into very thin
wire. It is too soft a metal to be used alone and hence
is alloyed with copper for general use. It is not acted
upon directly by oxygen and so does not tarnish in the
air unless sulphur be present. With sulphur it forms a
black compound. It is easily acted upon by nitric and sul-
phuric acids. At high temperatures it absorbs oxygen,
not combining with it however, and giving it off again
on cooling. Silver is used for coinage and for orna-
ments. Silver forms but one class of compounds, in
which it is univalent.

Gold

SYMBOL Au. ATOMIC WEIGHT 197.23

159. Occurrence.—Gold is found native. This free
gold may be in alluvial sands, or in quartz, or along with
copper and iron sulphids ("sulphurets").

160. Preparation.—The free gold may be separated
by means of the sorting power of water, or by mercury,
or dissolved out, after chlorination, with water, or dis-
solved with a dilute solution of potassium cyanid.

161. Properties.—Gold is a lustrous yellow metal with
a specific gravity of 19.3 and melting-point of 1037°. It
is the most malleable of the metals and can also be drawn
out into very fine wire. It is too soft to be used alone
and so is alloyed with copper or silver. Gold can only
be oxidized indirectly. It also resists the solvent action
of any single acid but can be dissolved by a mixture of
hydrochloric and nitric acids (*aqua regia*), by chlorin,
bromin, and by potassium cyanid. Gold is used for
coinage and jewelry. It forms two classes of com-

pounds : in the *aurous* it may be regarded as having a
valence of one; in the *auric* it is trivalent.

<div align="center">TABLE OF THE PROPERTIES OF GROUP I</div>

	Elements.	At. wt.	Sp. gr.	M. P.
Positive series..	Li	7.03	0.59	180°
	Na	23.05	0.98	96°
	K	39.11	0.87	58°
	Rb	85.43	1.5	39°
	Cs	132.89	1.88	27°
Negative series.	Cu	63.60	8.8	1090°
	Ag	107.92	10.5	1000°
	Au	197.23	19.3	1037°

GROUP VIII

Fe 56.02   Co 58.99   Ni 58.69

Ru 101.68   Rh 103.01   Pd 106.36

Os 190.99   Ir 193.12   Pt 194.89

The elements of this group arrange themselves clearly
into three series with similar increments of the atomic
weights in each series; or into three periods each with
three elements of nearly the same atomic weight. No
group element nor type element is known, unless, per-
haps, argon may belong to this group. According to the
best determinations, cobalt has a higher atomic weight
than nickel, whereas, according to the grouping of the
table, the reverse should be the case. This discrepancy
has not yet been explained. It may be due to imper-
fectly determined atomic weights or to some unknown
impurity present in one or the other element.

There is little justification in placing these three series
in a single group except that in physical properties the
elements resemble each other. While the members of
each series resemble each other quite closely, the
members of the different series diverge quite widely

from each other in chemical properties, especially in relation to oxygen.

Each forms a compound with oxygen in which it is bivalent, FeO, NiO, etc. All form also higher oxids in which their valence is increased, ruthenium and osmium forming oxids in which their valence appears to be eight; viz., RuO_4, and OsO_4. These elements will be considered in the horizontal series, thus taking together those of nearly the same atomic weight.

The Iron Metals

162. Occurrence.—The three light elements of the first horizontal series, if found free terrestrially, occur in traces only ; but many meteorites consist of iron alloyed with a small amount of nickel and less cobalt.

Iron occurs very abundantly as the sulphid, FeS_2, iron pyrites. This is not valuable as an ore of iron on account of the difficulty of removing the last traces of sulphur. The useful ores are the oxids: magnetite (Fe_3O_4), hematite (Fe_2O_3), limonite, brown hematite ($Fe_2O_3.xH_2O$) ; siderite, black band ore ($FeCO_3$). Iron is found in many silicates and other rocks. It is the coloring-matter of most soils and is present in the green coloring-matter of the leaves and in the blood of animals. Nickel and cobalt occur chiefly as sulphids, generally containing also arsenic, though found also as silicates, and in other minerals.

163. Preparation of Iron.—Iron is obtained from its ores by smelting in a blast-furnace. The ore, along with fuel (carbon) and a flux (limestone) for the removal of silica and such impurities, is placed in the furnace. The carbon monoxid, formed by the combustion of the carbon, reduces the iron ore giving metallic iron, which com-

bines with some of the carbon and melts, giving pig iron or cast iron. The first part of the reaction named would be indicated thus :

$$C + O_2 = CO_2 \; ; \; CO_2 + C = 2CO.$$
$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$
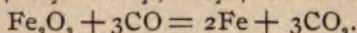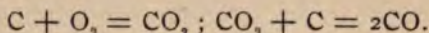
164. The Blast-furnace.—In the reduction of iron from its ores, or, as it is called, the smelting of iron, a blast-furnace is used. The accompanying figure (14) shows the construction of such a furnace. It consists of a brick stack covered with plates of boiler iron. It is usually ninety feet high by about twenty-five feet in diameter at the widest part (the bosh B). The materials are fed into the furnace at the top. They are : first the ore, second the fuel (coke or anthracite or charcoal), and third the flux (usually limestone). This flux is added to combine with the impurities of the ore (chiefly silica) forming slag or cinder.

165. The Blast.—The air needed for forming the carbon monoxid which reduces the iron ore, is forced into the furnace through several tuyeres placed around the circumference of the furnace and entering at the upper part of the crucible. These are protected from the great heat by water jackets (seen in Fig. 16). In some furnaces the entire crucible C is surrounded by such a jacket. The air-blast is heated in '' hot-blast ovens'' before entering the furnace. The melted slag swims upon the surface of the melted iron and so protects it from oxidation. It is drawn off regularly as it accumulates. The iron is also drawn off and cast in '' pigs.''
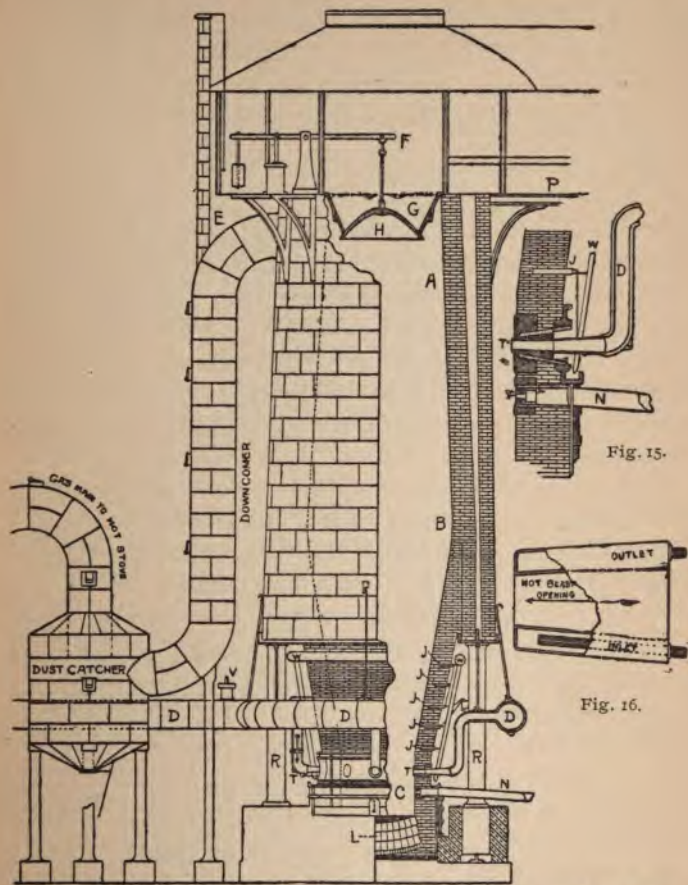
Fig. 14. The iron blast-furnace. A, Throat; B, Bosh; C, Crucible; D, Hot-
blast main; E, Bleeder for waste gas; G, Cup; H, Cone; I, Iron notch;
J, Bosh plates; N, Cinder trough; T, Tuyere; Y, Cinder notch.
Fig. 15. Shows the tuyere and cinder notch on a larger scale.
Fig. 16. Shows the tuyere on a larger scale.

166. Preparation of Nickel and Cobalt.—The first part of the preparation of these metals is troublesome because they have to be separated from the accompanying metals and then from one another. They are brought into the form of oxids and then reduced by heating with carbon.

$$NiO + C = Ni + CO.$$
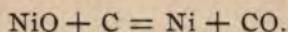
167. Properties.—The elements of this series are all lustrous white metals, quite hard and malleable. They fuse at the following temperatures: cobalt 1400°; nickel 1600°; iron 1900°. When pure they resist the action of oxygen at ordinary temperatures. At higher temperatures they oxidize more readily. Iron in its ordinary impure condition, oxidizes slowly in moist air ("rusting").

Iron is the most useful of all metals and is remarkable from the fact that when united with small quantities of carbon it assumes three different forms, the properties of each depending largely upon the relative amount of carbon present.

a. Wrought Iron contains less than 0.5 per cent. of carbon, is very tough, comparatively soft, fuses at a high temperature, and cannot be cast. It is easily worked by the hammer and welded when hot.

b. Cast Iron contains from 1.5 to 6 per cent. of carbon. It is brittle but very hard, fuses at a lower temperature than wrought iron, can be cast but cannot be welded. It can be made temporarily magnetic as can also wrought iron.

c. Steel has between 0.5 and 2 per cent. of carbon and may possess the most advantageous properties of both wrought and cast iron. Thus it may be very hard, may

be cast, welded, and may have great tensile strength. It may be tempered, that is, given a very tense and hard surface by sudden cooling. This temper is lost on reheating. It can be made permanently magnetic. The average specific gravity of iron is 7.8.

168. Steel Manufacture.—Most of the steel is at present made by the Bessemer process. This process consists in melting the pig iron, which is then run into a converter (Figs. 17–21). The converter is so arranged that a powerful blast of air enters at the bottom. The converter is tilted to receive the iron and then, as it is restored to the vertical position, the blast is turned on. This air passing through the melted iron burns out the carbon and silicon and oxidizes some of the iron, making it brittle. Enough of a cast iron, rich in manganese, is then introduced into the tilted converter to deoxidize this iron and add sufficient carbon to form steel. The blast is turned on again for a few moments when the converter is once more vertical. These converters hold about twenty tons and it requires fifteen or twenty minutes to convert this into steel.

Nickel and cobalt resemble iron in many of its properties but have a somewhat higher specific gravity, nickel 8.7 and cobalt 8.6. Cobalt is but little used in the metallic state; nickel is used in alloys and to plate over other metals; iron is chiefly used in the form of steel. All of these elements dissolve in dilute acids, nickel far less readily than the other two. Iron gives two classes of salts : *Ferrous*, in which it is bivalent, and *ferric* in which it is trivalent. Nickel and cobalt each give but one well-characterized class in which the metal is bivalent.

Experiment 78.—Test the fusibility of iron before the blow-pipe.

Fig. 19.

Fig. 18.

Fig. 17.
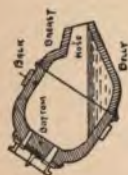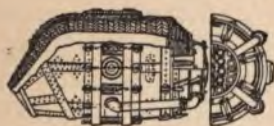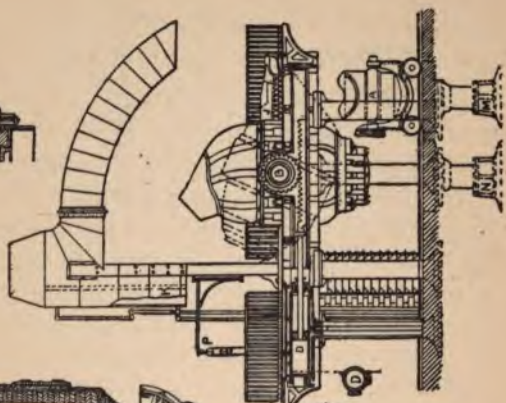
Fig. 21.

Fig. 20.

Experiment 79.—Test the action of iron upon dilute hydrochloric, sulphuric, and nitric acids. Is there any difference in the gases evolved? Dilute the solutions obtained and add sodium hydroxid to a small portion of each. Note any difference in precipitates. (The solution with nitric acid gives a ferric compound, the others ferrous.) Heat one of the ferrous solutions with a few drops of nitric acid, and repeat the test with sodium hydroxid. Has any change taken place? If so, what?

Experiment 80.—Test the solubility of nickel in dilute hydrochloric, sulphuric, and nitric acids.

Experiment 81.—Test the solubility of cobalt in dilute hydrochloric, sulphuric, and nitric acids. What difference is noted between the nickel and cobalt solutions?

The Platinum Metals

The two remaining series may be considered together. These elements are generally called the platinum metals. They occur together in the native or uncombined condition; ruthenium and osmium also occur very rarely as sulphids. Platinum forms rather more than nine-tenths of the purified ore and the other five elements the remainder.

169. Properties.—These are all white, lustrous, malleable and somewhat soft metals. They melt at temperatures ranging from 1500° to 2500°. Ruthenium, rhodium, and palladium have a specific gravity of 11 to 12 while osmium, iridium and platinum range from 21 to 22. These latter are the heaviest bodies in nature. Platinum is used in scientific laboratories and in connection with certain electrical appliances. The others are too rare to have important practical applications. With the exception of palladium, which is soluble in nitric acid, these elements cannot be dissolved by any single acid. They are however more or less soluble in a mixture of nitric and hydrochloric acids (*aqua regia*). The plati-

num metals do not oxidize at ordinary temperatures and some of them, as platinum, cannot be oxidized directly at any temperature, yielding oxids only by indirect methods. The classes of salts which they form will be mentioned under the head of their oxids.

TABLE OF THE PROPERTIES OF GROUP VIII

Elements.	At. wt.	Sp. gr.	M. P.
Fe	56.02	7.8	1900°
Co	58.99	8.6	1400°
Ni	58.69	8.7	1600°
Ru	101.68	12.2	(2000°)
Rh	103.01	12.1	(1900°)
Pd	106.36	11.4	1500°
Os	190.99	22.5	(2500°)
Ir	193.12	22.4	2000°
Pt	194.89	21.5	1775°

POSITIVE SERIES OF GROUP VII

Only one element is known in this series.

Manganese

SYMBOL, Mn. ATOMIC WEIGHT 55.

170. Occurrence and Properties.—This element shows many analogies to the iron series just described. In physical properties it shows little resemblance to the group type, chlorin, but certain classes of its compounds carry out the analogy. It forms no compound with hydrogen. Like iron it occurs chiefly in combination with oxygen. Several of these oxid ores are known. The most important is pyrolusite, MnO_2. It is also very commonly found in iron ores. It may be prepared ¦like iron by the reduction of its oxids with

carbon. Incidentally, it is reduced with the iron in iron ores and hence is present in ordinary iron and steel.

It resembles iron, being a hard, white, malleable metal with high fusing-point and a specific gravity of about 7. It oxidizes more easily than iron and dissolves easily in dilute acids. In its chief class of salts it is bivalent, in its highest oxid septivalent.

POSITIVE SERIES OF GROUP VI

Chromium

SYMBOL Cr.   ATOMIC WEIGHT 52.14.

171. Occurrence and Properties.—This is the most abundant element of this series. It occurs chiefly as chrome iron stone or chromite, a compound of its oxid with iron oxid, $Cr_2O_3.FeO$. It can be prepared from its oxid by reduction with carbon. It resembles iron in appearance, having a very high melting-point and a specific gravity of 6.7. It is oxidized with difficulty. It is soluble in dilute hydrochloric and sulphuric acids, but insoluble in nitric acid. Chromium is bivalent in some compounds, tri- and sexivalent in others.

Molybdenum

SYMBOL Mo.   ATOMIC WEIGHT 95.99.

172. Occurrence and Properties.—Molybdenum occurs as the sulphid, MoS, and as the molybdate of certain elements, $PbMoO_4$, etc. It is prepared by the reduction of the oxid by means of hydrogen at a high temperature. It melts at a very high temperature and has a specific gravity of 8.6. It oxidizes with diffi-

culty and is soluble in nitric acid but insoluble in the other common acids.

Tungsten

SYMBOL W. ATOMIC WEIGHT 184.83.

173. Occurrence and Properties.—This is also one of the comparatively rare elements. Its occurrence is very much like that of molybdenum, mainly as tungstate of certain elements, as $CaWO_4$, calcium tungstate; $FeWO_4$, ferrous tungstate; etc. The element is prepared by the reduction of the oxid by means of hydrogen. It melts at a high heat and has a specific gravity nearly as great as that of gold. It is oxidized somewhat more readily than molybdenum.

Uranium

SYMBOL U. ATOMIC WEIGHT 239.59.

174. Occurrence and Properties.—This element has the highest atomic weight of any of the elements. It is somewhat more abundant than the elements just mentioned and occurs chiefly in the form of oxid. The element is prepared by the action of sodium upon uranium chlorid. It can be melted at a white heat, has a specific gravity about the same as tungsten, and is easily oxidized when heated. It is soluble in dilute hydrochloric and sulphuric acids, but insoluble in nitric.

———

POSITIVE SERIES OF GROUP V.

V 51.38
|
Cb 93.73
|
Ta 182.84

Vanadium, Columbium, and Tantalum

175. Occurrence and Properties.—The elements of this series form well-characterized oxygen compounds in which they have a valence of five. Vanadium also acts with a valence of two, three, four, and six. They thus resemble nitrogen and phosphorus, the group element and the type element of this group. They are all rare elements, vanadium being more widely distributed and abundant than the other two. Vanadium is very widespread in its occurrence, but rarely occurs in more than traces. It is chiefly found as the vanadate of lead. Columbium and tantalum generally occur together as in columbite, a tantalate and columbate of iron, $Fe(CbTa)_2O_6$. These elements have been prepared by heating the chlorids in a stream of hydrogen. They oxidize readily to pentoxids when heated in the air. They are very difficult to dissolve in acids. Vanadium possesses some little importance technically, as in the dyeing industry.

Other Elements

176. Argon.—In the summer of 1894, Rayleigh and Ramsay discovered a new gas in the atmosphere. It forms about one per cent. of the air. The name argon has been given this gas because of its strange chemical inactivity. Its density is 19.9 and the molecule seems to consist of one atom. It has been condensed to a liquid. The general weight of opinion is in favor of considering this new substance an element. It has so far resisted all attempts to make it combine with the other elements, excepting certain ill-defined compounds with the hydrocarbons, and so nothing is known as to its

electrochemical character and valence, and its atomic weight is also in question.

177. Helium.—A little more than a year later one of the discoverers of argon, Ramsay, discovered another new gas which he named helium. This is obtained from a number of minerals, some of which contain it to the extent of several per cent. of their weight. It is also found in the gases of certain mineral springs. The density is about 2, and it also seems to have a monatomic molecule No compound of helium has been obtained, so we are still ignorant of its valence and chemical character, and the atomic weight is in doubt. By means of the spectroscope, helium has been identified with a substance occurring in the sun but hitherto unknown upon the earth and from this it receives its name.

Argon and helium are two of the most remarkable substances known to chemists and a fuller knowledge of them is awaited with great interest.

A number of other rare elements are known but have been imperfectly studied, and there are possibly others which remain to be discovered. Some of the better known of these rare elements are : **Gadolinium** (157), **erbium** (166), **neodymium** (144), **praseodymium** (140), **samarium** (150), **thulium** (171), and **ytterbium** (173).

PART III

HYDROGEN COMPOUNDS OF THE ELEMENTS, OR HYDRIDS

These compounds are called hydrids. With the exception of water, few of them occur in nature in more than traces. This is in strong contrast with the compounds of oxygen which are very abundant. Hydrogen being itself a positive element, forms compounds most readily with the strongly negative elements. The hydrids of the positive elements are imperfectly known and do not seem to be well characterized chemical substances. Most positive elements do not appear to form them at all. In studying these compounds therefore, the most negative group of elements will be taken up first. Most of these hydrids of negative elements are gaseous bodies (the higher hydrocarbons not being considered).

THE HYDRIDS OF GROUP VII

1. Hydrogen Fluorid, HF

178. Preparation.—From calcium fluorid by the action of sulphuric acid.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$
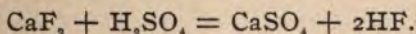
The preparation must be carried out in a platinum or leaden vessel as the compound attacks most other substances.

179. Properties.—It is a colorless gas with a pungent, irritating odor. It can be condensed to a liquid, boiling at 19° and having a specific gravity of 0.98. It is violently corrosive upon the skin and is very deadly in its action when breathed. It is very soluble in water and the solution is usually kept in bottles of ceresine or gutta percha.

Chemically it is very energetic, acting upon and dissolving many substances. Most interesting and useful is its action upon silica, even dissolving it away from many of its compounds. Thus it can be used for dissolving silica out of glass. This is called etching the glass. Hydrogen fluorid has strongly acid properties, an expression which will be more clearly defined further on. The solution in water is known as hydrofluoric acid.

2. Hydrogen Chlorid, HCl

This occurs sometimes in the gases issuing from volcanoes and dissolved in the water of certain streams in volcanic countries. Its energetic properties preclude its remaining long uncombined.

180. Preparation.—*a*. By the direct union of hydrogen and chlorin. This takes place under the influence of light.

$$H_2 + Cl_2 = 2HCl.$$
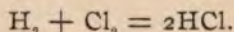
b. The action of sulphuric acid upon sodium chlorid sets free hydrogen chlorid. This is the common method of preparation.

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$
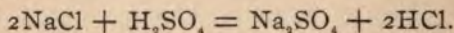
181. Properties.—It is a gas with a pungent suffocating odor, colorless and fuming strongly in moist air. It has a specific gravity of 1.26, may be condensed

to a liquid by a pressure of forty atmospheres and is a solid at —116°. It is very soluble in water, one volume dissolving 505 volumes of the gas at 0°. This solubility may be shown by inverting a tube full of the gas in a vessel of water (see Fig. 22) or by the same form of apparatus as is shown under ammonia. This solution
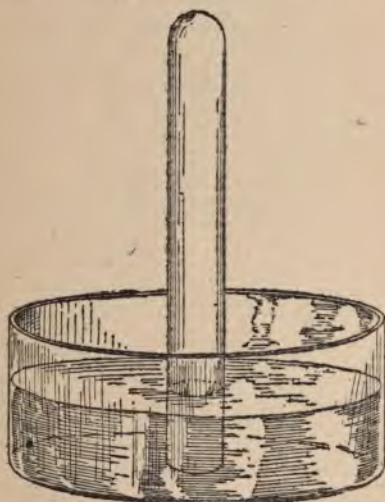
Fig. 22.

was formerly called muriatic acid because made from brine (muria). It is now called hydrochloric acid. This acid is produced in very large quantities and has many uses. A concentrated solution of hydrochloric acid in water has a specific gravity of 1.21 and contains about forty per cent. of hydrochloric acid by weight. Hydrogen chlorid will not support combustion, extinguishing a lighted taper. It acts very corrosively upon the mucous membrane, lining the throat and air passages, and so is very deadly when breathed. It is a very

stable compound and is only dissociated at a temperature of 1200°. It has strongly acid properties, dissolving a number of metals as iron, zinc, and aluminum, and combining with them to form chlorids.

3. Hydrogen Bromid, HBr

182. Preparation.—Hydrogen and bromin do not combine when placed together in the sunlight. Union of the two can be brought about by heating them, however. Pure hydrogen bromid cannot be prepared by the action of sulphuric acid upon sodium or potassium bromid as the strong sulphuric acid decomposes the hydrogen bromid in great measure as it is formed, and is, in its turn, reduced by the hydrogen set free. There is much less decomposition if a less easily reducible acid, like phosphoric, be substituted for the sulphuric acid.

$$2NaBr + H_3PO_4 = Na_2HPO_4 + 2HBr.$$
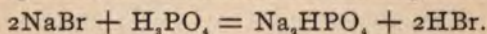
A better mode of preparation is by the action of phosphorus, bromin, and water.

$$P + 3Br + 3H_2O = P(OH)_3 + 3HBr.$$
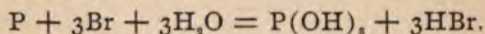
183. Properties.—This body resembles hydrogen chlorid quite closely. It is a colorless gas with a pungent odor and fumes strongly in the air. Its specific gravity is 2.79, and it is decomposed at a temperature of 800°. It extinguishes a taper and is poisonous. It is very soluble in water, the solution having the name hydrobromic acid. This solution dissolves some metals forming bromids. It is not so powerful a solvent as hydrochloric acid.

4. Hydrogen Iodid, HI

184. Preparation.—Hydrogen and iodin may be made to unite by careful and gentle heating of the two

together. This hydrid is so easily decomposed that it cannot be readily formed by the action of acids upon iodids. It is best formed by the action of phosphorus upon iodin and water.

$$P + 3I + 3H_2O = P(OH)_3 + 3HI.$$
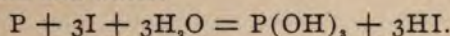
185. Properties.—It is a colorless gas with a pungent odor, fuming in the air. Its specific gravity is 4.41 and it is dissociated at 180°. It is very soluble in water, giving hydriodic acid. This has much less solvent power than the acids just mentioned. Its instability and the ease with which it breaks up into hydrogen and iodin give it a reducing action, or the power of removing oxygen from other substances. It is for this purpose that it is mainly used.

PROPERTIES OF THE HALOGEN HYDRIDS

Hydrid.	Density.	Mol. wt.	Phys. state.	Sp. gr. gas.	Temperature of condensation.	Per cent. in saturated solution.	Sp. gr. of solution.	Temperature of decomposition.
HF	10.	20.06	gas	0.69	—20°	35	1.15	....
HCl	18.2	36.45	gas	1.26	—80.3	40	1.21	1200°
HBr	40.5	80.95	gas	2.78	—73°	49	1.50	800°
HI	63.9	127.85	gas	4.41	—55°(solid)	58	1.71	180°

186. Acids and Bases.—These hydrids belong to a class of compounds known as *acids*. All acids contain hydrogen (one or more atoms) united to a negative element or negative group of elements (as in hydrochloric and sulphuric acids). The negative character predominates in acids and gives rise to certain general characteristics ; as a sour taste (when soluble), the changing of vegetable blues, as litmus to red, and the power of forming *salts*. When all or a part of the hydrogen of an acid is replaced by a

positive element or positive group of elements, a salt is formed.

$$Zn + 2HCl = ZnCl_2 + H_2;$$
$$ZnO + 2HCl = ZnCl_2 + H_2O.$$
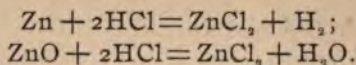
The element replacing the hydrogen of an acid to form a salt is often called a *base*, though the term base is more properly given to an oxid of a positive element. The soluble bases change vegetable reds to blue. When an acid is treated with a base so that its acid properties are lost, it is said to be *neutralized*, and *vice versa*. In each case a *salt* is formed. Acids with one replaceable hydrogen atom are called *monobasic*, as hydrochloric acid; with two, *dibasic*, as sulphuric acid; and with three, *tribasic*, as phosphoric acid, etc.

Experiment 82.—Prepare a glass plate (Fig. 23) by covering

Fig. 23.

with melted paraffin and after it has cooled, etching the paraffin partly off with a sharp point. Mix calcium fluorid (CaF_2) and concentrated sulphuric acid in a lead capsule, and cover with the glass plate, after having warmed the mixture in the dish till fumes of hydrofluoric acid gas (HF) begin to rise. After the hydrofluoric acid gas has acted on the glass a few moments, wipe the paraffin off the glass (warm the glass till the paraffin melts) and examine the etching on the glass.

Experiment 83.—Treat common salt (NaCl), in a flask provided with a safety tube (Fig. 6, p. 44), with concentrated sulphuric acid; warm gently; examine the gas evolved; let the gas pass into a test-tube partly filled with water. Is the gas soluble? Is its solution attended by heat? Examine the solution with litmus paper; evaporate a little upon platinum foil. Is it volatile? Treat a little of the solution with zinc (Zn) or iron (Fe). What takes place? what is evolved? Treat a little of the solution with sodium hydroxid (NaOH), noting the change which takes

place by the action on litmus paper. When exactly neutralized, taste the solution and compare with the taste of sodium hydroxid and of hydrochloric acid. Write all the formulas for the reactions in this experiment.

Experiment 84.—Take 10 cc. of normal (or equivalent) solution of hydrogen chlorid (hydrochloric acid, HCl) in a beaker; add enough litmus solution to color it distinctly pink (a few drops are sufficient); then add slowly from a burette normal (or equivalent) sodium hydroxid (NaOH) solution, with constant stirring until the solution is just changed to blue. What is the relative strength of the sodium hydroxid solution? After neutralization evaporate the solution in a porcelain dish, and examine the residue. What is it?

A normal (or equivalent) solution of a salt, acid, or base, is one that contains an " equivalent gram-molecule" to the liter ; that is, one gram of the substance for every unit of its molecular weight if it contains one hydrogen atom or its equivalent; one-half as much if it contains two hydrogen atoms or their equivalent, etc. For example :

$$\underbrace{Na\,O\,H}_{40}\underset{23+16+1}{} + \underbrace{H\,Cl}_{36.4}\underset{1+35.4}{} = NaCl + H_2O.$$
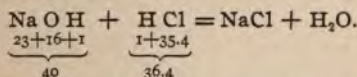
1 liter of normal sodium hydroxid solution will contain 40 grams sodium hydroxid per liter ; 1 liter of normal hydrogen chlorid solution will contain 36.4 grams hydrogen chlorid per liter ; and any quantity of normal hydrogen chlorid solution will be exactly neutralized by the same quantity of sodium hydroxid solution.

Again

$$\underbrace{2\,Na\,O\,H}_{80}\underset{2\times(23+16+1)}{} + \underbrace{H_2\,S\,O_4}_{98}\underset{2+32+64}{} = Na_2SO_4 + 2H_2O.$$
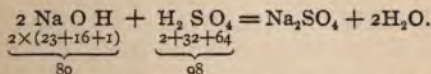
Since 1 liter of normal sodium hydroxid contains 40 grams per liter, it will be exactly neutralized by a solution of sulphuric acid (H_2SO_4) which contains $\frac{98}{2} = 49$ grams per liter, since sulphuric acid has two replaceable hydrogen atoms. Hence a normal solution of sulphuric acid will contain 49 grams per liter ; that is, one-half of the number of its units of molecular weight.

Experiment 85.—Test the laboratory solutions of hydrochloric

and sulphuric acids with normal sodium hydroxid, and the laboratory solution of sodium hydroxid, using normal hydrochloric acid solution, and determine their relative strength. How many grams of hydrochloric acid, sulphuric acid, and sodium hydroxid, are there in each of the respective solutions?

The only remaining member of the seventh group (manganese) forms no compound with hydrogen.

THE HYDRIDS OF GROUP VI

187. Oxygen Hydrids.—Oxygen forms two compounds with hydrogen, water, H_2O, and hydrogen dioxid, H_2O_2.

1. Hydrogen Monoxid, Water, H_2O

188. Occurrence.—This is one of the most abundant, simplest, and yet one of the most wonderful bodies in nature. As it is taken as a type, a clear understanding of its chemical nature is most important.

As has been said, this is the most widely distributed and most abundant compound in nature. 1. It covers much the larger portion of the surface of the earth and penetrates the crust of the part not covered by it. 2. It is in the atmosphere. 3. It is found in many minerals, as water of crystallization and hydration, and forms the larger part by weight of all plants and animals. It is so universally present that a chemist has to devote much time and ingenuity to its removal if he would free the bodies he works with from it and keep them perfectly dry.

189. Formation of Water.—*a*. When hydrogen or any of its compounds are burned in oxygen or in the air.

$$2H_2 + O_2 = 2H_2O.$$
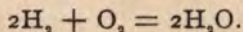
b. When compounds containing hydrogen are slowly oxidized. Thus water is formed in the respiration of

animals and in all decay of organic matter. *c.* In many chemical reactions, where hydrogen is a constituent of one molecule and oxygen of the other.

$$CuO + H_2 = Cu + H_2O.$$
$$CaO + H_2SO_4 = CaSO_4 + H_2O.$$
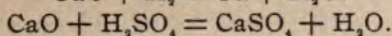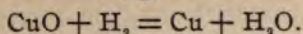
For the direct union of oxygen and hydrogen, an elevation of temperature is necessary. The temperature to which a body must be raised to unite with oxygen (burn) is known as its ignition-point or kindling temperature. When once the reaction has begun between hydrogen and oxygen it proceeds throughout the entire mixture with great rapidity, producing a violent explosion. A mixture of hydrogen and oxygen has, by pressure and lowering of temperature, been condensed to a colorless liquid, but without union of the hydrogen and oxygen.

An exact knowledge of the composition of water is very necessary for the science of chemistry. It is well then to examine into the proofs of its composition by volume and by weight.

190. Volumetric Composition. — 1. *By Analysis.*— When an electric current is passed through water it is decomposed into its two constituents, hydrogen and oxygen, and the volumes of each can be measured.

2. *By Synthesis.*—In this case an instrument called a eudiometer is used. This is a graduated tube near the top of which two platinum wires are introduced for the passage of electricity. Into this eudiometer a measured volume of oxygen is introduced and then more than twice as much hydrogen, also carefully measured. When this is exploded by means of the spark, it will be found that just twice as much hydrogen as the original volume of oxygen has combined with it and disappeared and that the excess of hydrogen is left unchanged.

191. Gravimetric Composition.—*By Synthesis.*—If a weighed amount of hydrogen be passed through a heated tube containing a weighed amount of copper oxid, the hydrogen will combine with the oxygen, leaving copper, and water will be formed. This water can be weighed and the weight of the copper remaining, subtracted from the weight of the copper oxid, will give the weight of the oxygen taken in forming the water. Thus the weights of the hydrogen and oxygen necessary to form a known weight of water are determined.

Experiment 86.—Mix in a wide-mouthed bottle two parts of hydrogen and one part of oxygen (from the cylinders). Wrap with a towel or thick paper and hold to a flame.

Experiment 87.—Hold a dry bottle or bell jar for a moment over a gas flame and note any deposit. (Coal gas contains hydrogen in combination.)

192. Properties.—Between 0° and 100° water is a liquid. Ice melts at 0° and water boils at 100° under 760 mm. pressure. Water follows the law of contraction from 100° down to 4°, at which temperature it has its maximum density. From this point down to 0° it expands and ice occupies a larger space than the water from which it is formed and hence floats upon it. The latent heat of water with reference to ice is 79 calories, and with reference to steam it is 536 calories. Water has a greater specific heat than any other body, and so is taken as the standard for specific heat. It is also the standard for the specific gravity of liquids and solids.

Water is nature's universal solvent. All substances are more or less soluble in it. In some cases the solubility is so slight that we speak of the bodies as being insoluble. Water is therefore never found pure in nature, but always contains more or less of the substances with which it has come in contact. Rain water

contains the dissolved gases of the atmosphere and, at
the beginning of showers, the dust which it sweeps down
from the air. In limestone regions spring and well
waters contain much calcium bicarbonate and often cal-
cium sulphate or gypsum. Such waters are called hard.
They do not form a lather with soap until all the calcium
salts have been precipitated by the soap as a curdy mass.
Magnesium also (combined in the same way as the cal-
cium) gives a hard water. Freestone waters have very
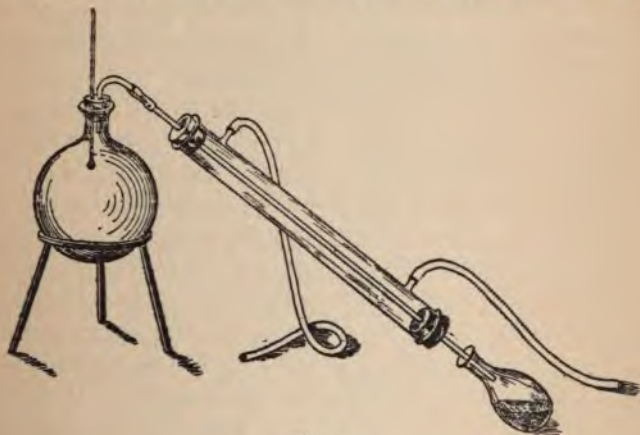
Fig. 24.

little mineral substance dissolved in them. Waters con-
taining sufficient substance dissolved to give an appre-
ciable taste and waters having a real or supposed thera-
peutic effect, are called mineral waters. In potable
waters the most dangerous impurity is organic matter,
especially disease germs. A well is a perpendicular
drain and hence is liable to contamination from neighbor-
ing surface drainage. Water may be purified partially by
filtration, thus freeing it from suspended water. It is much
more thoroughly purified by distillation (Fig. 24), free-

ing it from dissolved matter but not from volatile substances. Perfectly pure water can be prepared only with great difficulty. For drinking purposes water can be rendered harmless by boiling, at least so far as disease germs are concerned, as this destroys all such living organisms in the water.

Ordinary distilled water and the purest natural waters are blue when viewed through any considerable depth. Perfectly pure water is colorless, tasteless, and odorless. It would be called insipid by one drinking it, because we have become accustomed to the taste of ordinary water with its dissolved gases and mineral matter.

Water is a very stable compound, resisting dissociation up to 1800°. Heated to that temperature it breaks up into hydrogen and oxygen. Chemically, it is a neutral body; that is, the positive characteristics of the two hydrogen atoms are exactly balanced or neutralized by the negative characteristics of the one oxygen atom. It enters into a great many reactions and in most cases its presence seems to be essential in order that chemical action may take place. Thus many metals will not rust in dry air but easily rust if the air is moist. Ordinary illuminating gas will not burn if perfectly dry, nor can hydrogen be made to unite with oxygen if every trace of moisture be absent. The necessity for its presence in some of these cases is not yet fully explained. Water of crystallization and the phenomena of efflorescence and deliquescence have already been mentioned.

2. Hydrogen Dioxid, H_2O_2

This substance is found on analysis to contain twice as much oxygen as water. It was first prepared in 1818 by Thénard. It occurs in small quantities in the atmos-

phere and has been found in rain and snow. It is formed in a number of chemical reactions.

193. Preparation.—Decompose barium dioxid with dilute sulphuric acid.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$
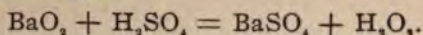
It is best to use the dehydrated dioxid and the mixture must be kept cold. The hydrogen dioxid is obtained in solution in water ; this can be concentrated with difficulty. It has, however, been prepared free from water.

194. Properties.—It forms a colorless, oily liquid. The specific gravity is about 1.5. It evaporates slowly *in vacuo* and does not solidify at a temperature of —30°. It has no smell but has an astringent bitter taste and produces a blister if brought upon the skin, which may result in a painful sore. Chemically, it is a very unstable body, decomposing into oxygen and water. On heating a concentrated solution this decomposition takes place with almost explosive violence. It bleaches organic coloring-matters and is largely used for this purpose. This is due to the oxygen given off. It liberates iodin from potassium iodid, and decomposes ozone, forming oxygen and water.

$$H_2O_2 + O_3 = H_2O + 2O_2.$$
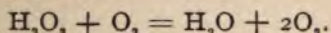
It is used as an oxidizing agent, and because of its destructive action upon organic matter, is used as a disinfectant. Hydrogen dioxid is ordinarily used in a dilute aqueous solution which evolves from ten to fifteen times its volume of oxygen on being heated and is known as a ''10 volume'' ($2\frac{2}{3}$ per cent.), a '' 15 volume'' (4 per cent.) solution. Owing to its slow decomposition, even at ordinary temperatures, this solution can be preserved only a short time. In a few months it will have com-

pletely decomposed. It is also used for bleaching or "blondining" the hair.

Hydrogen dioxid may also act as a reducing agent, as

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2,$$
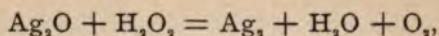
where its normal oxidizing action is exerted upon the oxygen of the silver oxid and the silver is liberated.

Its graphic formula may be represented as

$$\underset{H}{\overset{H}{\diagdown}}\overset{\text{iv}}{O}{=}O \text{ or } H{-}O{-}O{-}H.$$
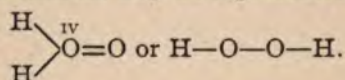
195. Sulphur Hydrids.—Sulphur also forms two compounds with hydrogen, hydrogen sulphid, H_2S, and hydrogen disulphid, H_2S_2.

1. Hydrogen Sulphid, H_2S

196. Occurrence.—This is found free in the water of sulphur springs. It is formed in nature by the decomposition of metallic sulphids and of organic matter containing sulphur.

197. Preparation.—It is best prepared by the action of dilute acids upon certain metallic sulphids, as for instance, sulphuric acid upon ferrous sulphid.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$
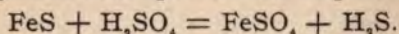
It can also be prepared by passing hydrogen over heated sulphur or sulphids.

198. Properties.—It is a colorless, bad-smelling gas, with a sweetish taste. It is quite soluble in water, so that it cannot be collected over it; its specific gravity is 1.17; at $-62°$ it condenses to a liquid and at $-85°$ it freezes to an ice-like solid; it is poisonous, producing unconsciousness and death when breathed. It is much

less stable than the corresponding oxygen compound, H_2O. Heating to $400°$ causes its dissociation and its solution in water is slowly decomposed by air,

$$H_2S + O = H_2O + S,$$
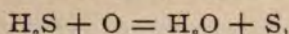
or immediately by the halogens,

$$H_2S + Cl_2 = 2HCl + S.$$
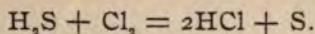
This solution cannot therefore be preserved very long. It has a slight acid character and can be used to precipitate the metallic sulphids. It is accordingly much used in analysis. The gas burns with a blue flame. If, however, the oxygen present is insufficient for complete combustion, the hydrogen burns and the sulphur is separated in the solid form.

Experiment 88.—Perform this experiment in the fume room. Treat a piece of ferrous sulphid (FeS) with sulphuric acid. Examine the gas evolved as to odor, appearance, and combustibility. Attach a delivery-tube and lead the gas into water in a test-tube. Add the solution of hydrogen sulphid (H_2S) thus obtained, to solutions of lead nitrate ($Pb(NO_3)_2$), cadmium sulphate ($CdSO_4$), antimony chlorid ($SbCl_3$), and mercuric chlorid ($HgCl_2$). Write the formula for each reaction.

2. Hydrogen Disulphid, H_2S_4

199. Preparation and Properties.—This substance can be prepared by a reaction similar to the one used for the preparation of hydrogen dioxid.

$$CaS_2 + 2HCl = CaCl_2 + H_2S_2.$$
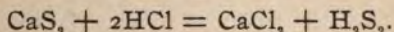
It is a liquid, unstable, decomposing into hydrogen sulphid and sulphur. It has a disagreeable odor and some bleaching power. It is poisonous. In these properties its analogy to hydrogen dioxid is seen.

200. Selenium Hydrid.—Selenium forms but one com-

pound with hydrogen, hydrogen selenid, corresponding
to the types H_2O and H_2S.

Hydrogen Selenid, H_2Se

201. Preparation and Properties.—The preparation is
similar to that of the corresponding sulphur compound.

$$FeSe + 2HCl = FeCl_2 + H_2Se.$$
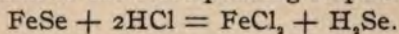
It is a colorless gas with a smell like that of hydro-
gen sulphid but more persistent and intolerable. It is
more soluble in water, giving a faintly acid solution,
which is decomposed by the oxygen of the air, and it
precipitates metallic selenids. It is nearly three times
as heavy as air and burns with a blue flame.

202. Tellurium Hydrid.—Tellurium forms but one
compound with hydrogen, hydrogen tellurid, H_2Te, cor-
responding to the types H_2O and H_2S.

Hydrogen Tellurid, H_2Te

203. Preparation and Properties.—It is prepared by
the action of an acid upon a metallic tellurid.

$$ZnTe + 2HCl = ZnCl_2 + H_2Te.$$
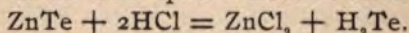
It is heavier than the preceding gases and has anal-
ogous properties.

PROPERTIES OF THE HYDRIDS OF GROUP VI

Compound.	Molecular weight.	Phys. state.	Specific gravity.	Dissociation temperature	Reaction.
H_2O	18	liquid	1	$1800°$	neutral
H_2O_2	34	liquid	1.5	$100°$	neutral
H_2S	34.06	gas	1.17(air)	$400°$	acid
H_2S_2		liquid		ord. temp.	acid
H_2Se	80.87	gas		$150°$	acid
H_2Te	139.70	gas		low temp.	acid

THE HYDRIDS OF GROUP V

204. Nitrogen Hydrids.—Nitrogen forms three compounds with hydrogen, ammonia NH_3, hydrazin N_2H_4, hydrazoic acid, N_3H. Two other compounds are known which belong to the class of salts.

1. Ammonia, NH_3

205. Occurrence.—Ammonia is found in the air in the form of carbonate and also as nitrite and nitrate. Here it is a very small but essential constituent. In combination with nitrous and nitric acids it is found in rain water and snow. Its compounds are found in volcanic districts and it is a necessary constituent of all fertile soils. It gets into the various natural waters from the soil or atmosphere. The ammonia thus occurring in atmosphere, soil, and water comes from the decay of nitrogenous organic matter, and also, perhaps, from the action of electricity upon nitrogen and water. Ammoniacal salts are also found in the juices of plants and in most animal fluids, especially in decomposed urine.

206. Preparation.—When any compound of ammonia is treated with a strong base like lime, the ammonia is liberated.

$$2NH_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O.$$
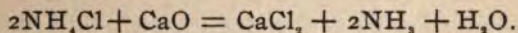
The compounds of ammonia are usually obtained by the distillation of coal, bones, or other complex organic substances containing nitrogen. If these nitrogenous materials are allowed to decay, with partial exclusion of air, some of the nitrogen is obtained in the form of ammonia. Sal ammoniac was the name given to one of the earliest compounds of ammonia known, the chlorid, prepared by the distillation of camel's dung with salt.

Spirits of hartshorn was the name for the ammonia obtained by the distillation of the bones of deer. Both of these names are still used to some extent. Ammonia gas was discovered by Priestley in 1774 and called alkaline air. Commercially, most of the ammonia is at present obtained in the purification of coal gas.

For purposes of experiment, ammonia may be prepared by heating its aqueous solution in a flask and catching the gas driven off.

207. Properties.—Ammonia is a gas with a very pungent odor and alkaline taste. The gas can be condensed by a temperature of $-40°$ and becomes solid at $-75°$. It can be made to burn, though with some difficulty. Liquefied ammonia is used in the manufacture of artificial ice, its evaporation abstracting the heat from surrounding objects. The gas has a specific gravity of 0.59 and is very soluble in water (1148 volumes dissolving in one volume at $0°$). This great solubility may be strikingly shown by the use of the apparatus in Fig. 25. The tube is filled with ammonia and if a little red litmus water be forced into it by blowing into the flask, the fountain will continue to play of itself from the pressure of the atmosphere. The solution of this gas is called *aqua ammonia*. It acts

Fig. 25.

like one of the alkaline hydroxids, and so is spoken of as containing ammonium hydroxid, NH_4OH. This substance has, however, never been isolated. Chemically the gas is basic in nature, turning litmus blue and form-

ing a number of compounds by combining with the acids; thus:

$$N{-}H + HCl = Cl{-}N\begin{smallmatrix}H\\H\\H\\H\end{smallmatrix} \text{ or } NH_4Cl,$$
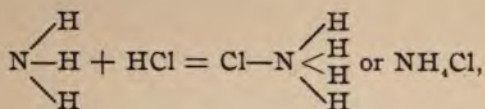
208. The Ammonium Radical, $-NH_4$ or $-N\begin{smallmatrix}H\\H\\H\\H\end{smallmatrix}$,

is a hypothetical radical, incapable of independent existence; it resembles a positive element (especially sodium and potassium), and is called ammonium. The existence of this compound radical, a molecule made of several atoms, yet behaving in many respects like the single atom of an element, seems a clue to the nature of the elements. Regarded as an element it would fall in the first group among the alkalies. Ammonia, or NH_3, was long known as the volatile alkali. The most important compounds of ammonium with the acids are the carbonate (sal volatile), chlorid (sal ammoniac), nitrate, and sulphate. Nearly all of the ammonium compounds are soluble in water.

Experiment 89.—Rub together in the palm of the hand small quantities of ammonium chlorid (NH_4Cl) and lime (CaO). What is evolved?

Experiment 90.—To a solution of ammonium chlorid in a testtube add a solution of sodium hydroxid. Warm and examine the evolved gas. Test its effect on moist litmus paper and on the stopper of the hydrochloric acid bottle. What are the fumes in this last case?

Experiment 91.—Neutralize a solution of ammonium hydroxid (NH_4OH) with sulphuric or hydrochloric acid, using litmus as an indicator. Evaporate the solution. What is found?

Experiment 92.—Neutralize the laboratory solution of ammonium hydroxid (NH_4OH) with normal hydrochloric acid solu-

tion, using litmus as an indicator, and determine its strength. Evaporate the neutralized solution. What is found? How many grams of ammonium hydroxid in a liter of the laboratory solution? See Experiment 84, p. 113.

2. Hydrazin or Diamid, N_2H_4 or $\begin{matrix} N{<}^H_H \\ | \\ N{<}^H_H \end{matrix}$
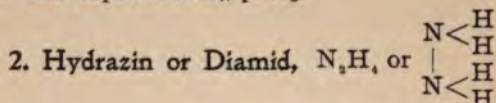
209. Preparation.—This substance is prepared by an indirect method. It is obtained by boiling triazoacetic acid with sulphuric acid, this giving a salt, hydrazin sulphate, from which the hydrazin is liberated by means of a strong base.

210. Properties.—It is a gas closely resembling ammonia, with a peculiar penetrating odor, very soluble in water. Its hydroxid is very caustic, attacking glass. It is basic and forms compounds with acids.

3. Hydrazoic Acid, HN_3

211. Preparation.—When sodium is treated with ammonia, sodamid is formed.

$$Na + NH_3 = NaNH_2 + H.$$
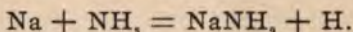
This is then treated with nitrogen monoxid.

$$NaNH_2 + N_2O = H_2O + NaN_3.$$
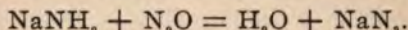
An acid will set free the hydrazoic acid.

$$2NaN_3 + H_2SO_4 = Na_2SO_4 + 2HN_3.$$
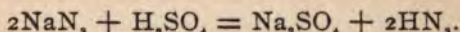
212. Properties.—It is a colorless, mobile liquid with a very pungent, unpleasant smell. It is poisonous, very unstable, and decomposes with great violence at times. It has an acid character, or the opposite to that of ammonia, somewhat resembling hydrochloric acid, combining with bases. These salts are explosive.

213. Phosphorus Hydrids.—Three compounds of phosphorus with hydrogen are known : phosphin, PH_3, liquid hydrogen phosphid, P_2H_4, and solid hydrogen phosphid, P_4H_2.

1. Phosphin, PH_3

214. Preparation.—It may be prepared by the action of calcium phosphid upon water. Or it is obtained by the action of caustic potash upon phosphorus and water.

$$3KOH + P_4 + 3H_2O = 3KH_2PO_2 + PH_3.$$
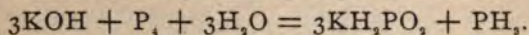
In heating the phosphorus with the solution of potas-

Fig. 26.

sium hydroxid, care must be taken to exclude air, as, for instance, by a stream of carbon dioxid (see Fig. 26), and the exit tube must end under water.

215. Properties.—It is a colorless gas, with a peculiar, unpleasant odor, somewhat soluble in water, giving a caustic taste. It is a little heavier than air, ignites at 100°, is easily decomposed by heat, very poisonous, basic, and forms a few compounds with acids. It burns to white fumes of phosphorus pentoxid, P_2O_5.

2. Liquid Hydrogen Phosphid, P_2H_4

216. Preparation and Properties.—This body is prepared at the same time with the gaseous one by the reactions given above. It can be separated by careful cooling of the products as they are given off, thus obtaining it in the form of a liquid.

It is a very unstable liquid, inflammable at ordinary temperatures, and is decomposed by slight heating or by exposure to the light. Its presence in phosphin, as ordinarily prepared, causes it to be spontaneously inflammable.

3. Solid Hydrogen Phosphid, P_4H_2

The existence of this body has been questioned. No definite mode of preparation can be given. Its exact composition and nature are also unknown. It seems to be a yellow powder, decomposed by heating to 70°, and taking fire in the air at 100°.

217. Arsenic Hydrids. — Arsenic forms two compounds with hydrogen : arsin, AsH_3 and solid hydrogen arsenid, As_2H_2.

1. Hydrogen Arsenid or Arsin, AsH_3

218. Preparation.—Zinc arsenid, when treated with dilute sulphuric acid, gives arsin.

$$As_2Zn_3 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4.$$
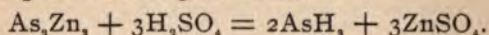
This gives pure arsin. It may be prepared, mixed with hydrogen, by the action of nascent hydrogen upon compounds of arsenic.

$$As_2O_3 + H_{12} = 2AsH_3 + 3H_2O.$$
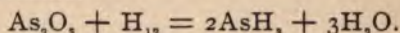
Thus, when an arsenic compound, or a body containing

arsenic, is introduced into a flask where hydrogen is being generated (by zinc and sulphuric acid, for instance), arsin is formed.

219. Properties.—Arsin is a gas more than twice as heavy as air. It can be liquefied at —40°, is very poisonous, and is somewhat soluble in water ; this solution decomposes on standing in the air. The gas burns with a pale bluish flame, emitting clouds of arsenic trioxid. When the flame is cooled by the introduction of a cold object the hydrogen continues to burn but the arsenic is deposited. The gas is easily decomposed by heating. The formation of arsin is used as a delicate test for arsenic.

2. Solid Hydrogen Arsenid, As_2H_2

This is a brown silky substance whose existence as a distinct chemical compound is uncertain.

220. Antimony Hydrid.—Antimony forms but one compound with hydrogen, stibin, SbH_3, which is analogous to the type NH_3.

Hydrogen Antimonid or Stibin, SbH_3

221. Preparation and Properties.—This body is prepared (analogous to arsin) by the action of nascent hydrogen upon a soluble antimony compound. This gives the gas mixed with hydrogen from which it has never been entirely separated. The gas seems to be very unstable unless largely mixed with hydrogen. It has a disagreeable smell and taste and is poisonous. It is about as soluble in water as arsin. It burns with a grayish blue flame, evolving white fumes of antimony trioxid while burning, and depositing antimony upon any cool object introduced into the flame. It is also decom-

posed by heat but with somewhat greater difficulty (when mixed with hydrogen) than arsin. Stibin precipitates a few metallic antimonids from solution.

PROPERTIES OF THE HYDRIDS OF GROUP V

Compound.	Molecular weight.	Phys. state.	Specific gravity.	Boiling-point.	Solubility.	Reaction.
NH	17.04	gas	0.59	$-35°$	1148 vols : 1	strong base
N$_2$H$_4$		gas			sol.	base
N$_3$H		liquid		$37°$	sol.	acid
PH$_3$	34.02	gas	1.18	$-85°$	sol.	base
P$_2$H$_4$	66	liquid		$30°$		
P$_4$H$_2$		solid				
AsH$_3$	78.01	gas	2.69	$-40°$	5 vols : 1	neutral
As$_2$H$_2$		solid				
SbH$_3$	123.43	solid	4.3	$-18°$	4 vols : 1	neutral

THE HYDRIDS OF GROUP IV

222. Carbon Hydrids.—Carbon forms a very large number of compounds with hydrogen. These are called hydrocarbons. Many of them occur naturally in petroleum, natural gas, etc. They will be studied under the head of Organic Chemistry. There are two especially important and typical hydrocarbons which will be briefly treated here. These are methane, CH_4, and acetylene, C_2H_2. The first is the typical hydrid of the group.

1. Methane, CH_4

223. Occurrence.—This is found in a great many places where vegetable matter is undergoing slow decay with partial access of oxygen. It is formed by organic matter decaying beneath the water, or deep under the soil. In the first case it is called marsh-gas; in the latter the fire damp of the mines. It is the principal constituent of the natural gas drawn from deep borings in various parts of the earth.

224. Preparation.—Methane is prepared by heating together sodium acetate and sodium hydroxid.

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$
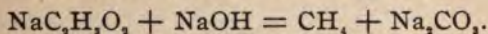
225. Properties.—It is a colorless gas with a slight smell and somewhat soluble in cold water. It is very difficult to condense and for a long time was counted among the permanent gases. It burns with a slightly luminous flame and explodes when mixed with air or oxygen in the proper proportions and heated. Chemically, it is not acid nor yet strongly basic. On giving up one of its hydrogen atoms a positive radical, CH_3, is left.

2. Acetylene, C_2H_2, or $H—C≡C—H$.

226. Preparation.—This hydrocarbon can be produced

by decomposing complex organic bodies by means of heat. It can also be obtained by the action of electricity upon carbon surrounded by hydrogen. It is more easily prepared by allowing water to act upon calcium carbid.

$$CaC_2 + H_2O = C_2H_2 + CaO.$$
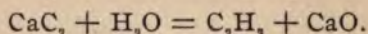
227. Properties.—This also is a gas burning with a very brilliant light, or if abundance of oxygen is not supplied, with a smoky flame. It explodes when a mixture with oxygen, or air, in the proper proportions, is heated. It has the power of uniting directly with the halogens, without giving up any hydrogen.

Experiment 93.—Treat a small piece of calcium carbid (CaC_2) with water in a test-tube. Examine the evolved gas. What is it? What kind of a flame does it burn with? Why?

228. Flame.—It will be convenient here to discuss the nature and structure of flame. Flame is ordinarily caused by the combustion of gas. The amount of light given off is determined not by the temperature mainly but by the density of the gases and the presence of solid incandescent particles. In the burning of a solid, as a piece of wood or coal or a candle, we have first the formation of a gas and then the burning of this gas.

229. Kindling Temperature.—It is noteworthy, first, that the gas cannot burn unless it is heated up to a certain temperature which is called the kindling temperature. If a burning gas is cooled down below this temperature it will cease to burn. Thus a burning gas may be cut off by a piece of wire gauze (see Fig. 27), and the flame cannot go beyond the gauze until the meshes have been heated up sufficiently to ignite the gas on the other side. This is the principle of the Davy lamp (see Fig. 28), for use by miners. It is, however, still possible in some cases, at the reduced temperature, for a flameless combus-
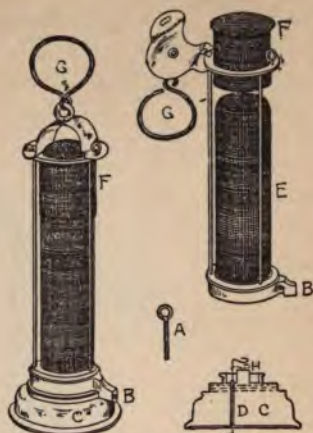
Fig. 27.   Fig. 28.

tion to go on. In many cases a compound gas may be
so cooled that a portion of its constituents can-
not continue to burn, although the rest does.
Thus a cold object placed in the flame of a
lamp or a gas jet will quickly become coated
with carbon while the hydrogen of the gas
still burns. This is true of a number of gases
as hydrogen sulphid, arsin, stibin, etc.

230. Structure of Flame. — A gas flame
can be divided into three parts: an inner zone
a (Fig. 29) of unburnt gas in which the tem-
perature is low ; a flame, giving colored zone
b, outside this, in which there are incandescent
particles of carbon and where there is a mod-
erately high temperature—this is the zone of
incomplete combustion ; and lastly, an outer
blue zone c, where the combustion is complete
and the temperature highest. The yellow zone or flame

Fig. 29.

is called a reducing flame because it contains an excess
of carbon which will remove oxygen from reducible
bodies placed in it.   The blue or colorless flame is called

Fig. 30.

an oxidizing flame, containing an excess of oxygen and
so oxidizing bodies heated in it.   The oxidizing and redu-
cing flames may also be produced,
with a higher temperature, by the
use of a blowpipe (see Fig. 30).

Experiment 94.—Direct the blowpipe
flame on a small piece of lead on char-
coal.   Notice the different effect of the
oxidizing and the reducing flames.
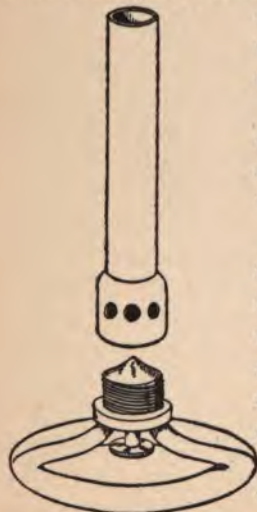
231. The Bunsen Burner.—In
this burner the gas is admitted
through a jet just at the base of a
tube acting as a chimney.   This
chimney is so arranged that through
openings a greater or less amount
of air may be admitted and swept
up with the entering gas.   Thus a
very rapid intense combustion of the
gas may be secured or one less
intense as desired (see Fig. 31).

Fig. 31.

232. Silicon Hydrid.—Silicon and hydrogen unite to form but one compound and this has the typical composition, SiH_4.

Silicon Hydrid, SiH_4

This substance is prepared by the action of hydrochloric acid upon a compound of silicon and magnesium.

$$SiMg_2 + 4HCl = SiH_4 + 2MgCl_2.$$
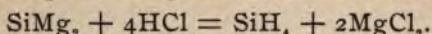
233. Properties.—It is a gas, colorless, heavier than air, spontaneously inflammable in the air when mixed with hydrogen, and quite stable as it is decomposed only at a red heat.

234. Valence as Illustrated in the Hydrids.—The compounds which we have studied enable us to form a fuller idea of the property of valence. It is, as we have learned, the quantitative combining power of the elements. Thus, taking the group elements, the following series of the compounds of hydrogen have been studied: HF, H_2O, H_3N, H_4C. The elements of the different groups evidently have a different power for combining with hydrogen, ranging from one to four atoms of hydrogen to the single atom of the element. It is clear that, in measuring this quantitative combining power, some element must be taken as the standard. Hydrogen is taken as the standard and the combining power, or valence as it is called, is measured by the number of hydrogen atoms with which one atom of the element will combine. Thus fluorin combines with one atom of hydrogen and so its valence is one or it is a univalent element; oxygen is bivalent; nitrogen is trivalent; and carbon is quadrivalent. This valence is not distinctively the property of one element, but represents the resultant of the mutual influence of the hydrogen

and the element in question. As this influence changes it is possible for the valence of an element to change. It will be noted that the valence of the elements with reference to hydrogen increases regularly from one in Group VII to four in Group IV. From there on it decreases until it is one again in Group I. The elements of the first three groups form few well-characterized compounds with hydrogen, hence in determining their valence some other element of the same valence as hydrogen may be used. Thus with reference to chlorin the valence by groups decreases from four in Group IV to one in Group I.

Oxygen is also used to measure the valence of the elements but this will be referred to again after the study of the compounds of oxygen.

235. Formation of Hydrids.—It will be noticed that many of the compounds of hydrogen are formed by the same general reaction; *viz.*, treating with an acid a compound of the negative element with some element more positive than hydrogen.

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$
$$CaC_2 + 2HCl = CaCl_2 + C_2H_2.$$
$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4.$$
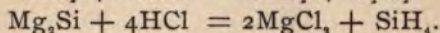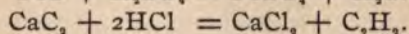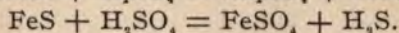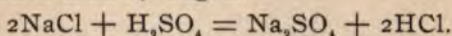
Sulphuric acid is generally used for this reaction as it is the strongest of the common acids, but it may, in many cases, be replaced by weaker acids, and even, as in the last two reactions, by water.

$$CaC_2 + 2HOH = Ca(OH)_2 + C_2H_2.$$
$$Mg_2Si + 4HOH = 2Mg(OH)_2 + SiH_4.$$
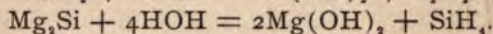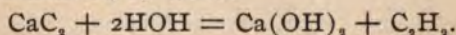
PART IV

HALOGEN COMPOUNDS OF THE ELEMENTS, OR HALIDS

Having studied the compounds of hydrogen we will next consider the binary compounds formed by the elements of Group VII, or the halogens, with those of the other groups.

236. The Halids.—These elements, fluorin, chlorin, bromin, and iodin form compounds with all the elements. Owing to the strongly negative character of these elements, the compounds with the more positive elements are much more stable than those with the more negative elements; *e. g.*, NaCl, stable; Cl_2O, unstable. The compounds of fluorin, chlorin, bromin, and iodin are respectively fluorids, chlorids, bromids, and iodids. These compounds with the more positive elements are salts and are generally soluble in water, exceptions being the chlorin, bromin, and iodin compounds of silver, copper (cuprous), gold (aurous), mercury (mercurous), lead, thallium (thallous), and platinum (platinous); and the fluorids of copper, calcium, strontium, and barium.

These compounds may be formed as follows:

237. Formation of the Halids.—1. By the action of chlorin, bromin, or iodin on the elements; *e. g.*,

$$Zn + Cl_2 = ZnCl_2.$$
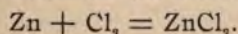
2. By the action of the halogen acids, hydrofluoric, hydrochloric, hydrobromic, or hydriodic, upon the elements, their oxids, hydroxids, etc.; $e.\,g.$,

$$Zn + 2HCl = ZnCl_2 + H_2;$$
$$ZnO + 2HCl = ZnCl_2 + H_2O.$$
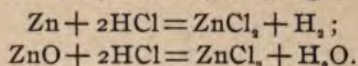
3. By the action of chlorin and carbon on the oxids of the elements at a high temperature :

$$3Cl_2 + Al_2O_3 + 3C = 3CO + 2AlCl_3.$$
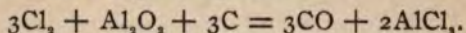
4. By double decomposition in the case of insoluble halogen salts:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$
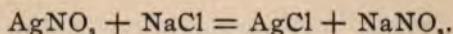
The more important compounds of these elements will be considered in the order of the groups beginning with Group I, and along with that group the compound radical ammonium will be included.

THE HALIDS OF GROUP I

238. The Halids of the Positive Series.—Sodium fluorid (NaF), potassium fluorid, and ammonium fluorid, are soluble crystalline bodies and are used as fluxes. Lithium chlorid (LiCl), sodium chlorid, potassium chlorid, rubidium chlorid, cesium chlorid, as well as the other halogen compounds of these elements, are all easily soluble in water.

Sodium chlorid (NaCl), common salt, is the chief alkaline chlorid and is the most abundant mode of occurrence of both sodium and chlorin. It occurs dissolved in the water of lakes, seas, salt springs, etc. ; also in extensive mines and salt deposits, which may have been formed from the drying up of prehistoric seas. From the sea it is often carried up into the atmosphere

so that small amounts may be found in the air many miles inland. It is also found in small amounts in most soils and inland waters. It is a constituent of most animal secretions and is necessary to animal life. It is a white body, crystallizing in cubes and about equally soluble in hot and cold water. It is stable up to a very high temperature. It can be melted and volatilized. It is used as a food also in glass-making, glazing pottery, in preparing sodium compounds and in many other ways.

Potassium chlorid (KCl) is very often found along with sodium chlorid though it is not so abundant. It is similar to it in many ways. It is used for preparing the other compounds of potassium.

Experiment 95.—Neutralize a solution of potassium hydroxid with hydrochloric acid and evaporate. Repeat, using sodium hydroxid in place of potassium hydroxid. Compare the two salts obtained on evaporation. What are they?

Experiment 96.—How much hydrochloric acid (by weight) will be required to neutralize 10 grams of potassium hydroxid? To neutralize 10 grams of sodium hydroxid?

Potassium bromid and potassium iodid are the chief salts of bromin and iodin. They are prepared by the action of bromin (or iodin) on iron in water forming the bromid (iodid) of iron, which is then decomposed by potassium carbonate.

$$Fe + I_2 = FeI_2 ; FeI_2 + K_2CO_3 = FeCO_3 + 2KI.$$
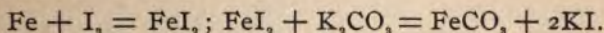
The solution is then evaporated and the potassium bromid or iodid purified by recrystallization. These salts, potassium bromid and potassium iodid, are extensively used in medicine and in photography.

Experiment 97.—Put about 0.5 gram of iodin in a test-tube with two or three nails; cover with water and set away for at least twenty-four hours. Then (or when the liquid has lost its brown color) pour it into another test-tube and add potassium

carbonate solution until it is just alkaline. Filter the solution and evaporate. What is formed ? Write formulas for reactions. How much of the salt could be obtained from 0.5 gram of iodin? Save the salt formed.

239. The Halids of the Negative Series.—The chlorin, bromin, and iodin compounds of these elements in their univalent form, *viz.*, cuprous chlorid, silver chlorid, and aurous chlorid, are insoluble in water. Copper, however, has a strong tendency to act as a bivalent element and the compound $CuCl_2$ (cupric chlorid) is a blue, very soluble salt. Gold also forms a soluble chlorid, in which it acts as a trivalent element ($AuCl_3$).

Silver chlorid, when formed by precipitation from a silver salt by a soluble chlorid (*e. g.*, $AgNO_3 + HCl = AgCl + HNO_3$), is a white, curdy solid, which rapidly darkens with loss of chlorin when exposed to light. The art of photography depends upon this change, and others which are analogous.

Experiment 98.—To a few drops of silver nitrate ($AgNO_3$) solution add hydrochloric acid. What is formed? Test its solubility in ammonium hydroxid (NH_4OH).

Cupric fluorid is insoluble. It is used to coat over copper vessels for receiving fluorin so that they will not be attacked by it.

THE HALIDS OF GROUP II

240. The Halids of the Positive Series.—The most important fluorid is that of calcium (CaF_2). This is found widely distributed and quite abundant, under the name of fluor spar or Derbyshire spar. It is often very beautifully crystallized and variously colored by impurities present. It is the source of all the compounds of fluorin. It is used for the preparation of

hydrofluoric acid in etching, and as a flux. The fluorids of the Positive Series (calcium, strontium, and barium fluorids), are insoluble in water; the other halogen compounds are soluble and magnesium, calcium, and zinc chlorids are deliquescent. Magnesium chlorid ($MgCl_2$) occurs in seawater and renders the crude salt obtained on its evaporation deliquescent and bitter. It is decomposed by heating and by steam. Owing to its great affinity for water, calcium chlorid is used as a drying material for liquids and gases.

241. The Halids of the Negative Series.—Zinc chlorid is used as a dehydrating substance in organic chemistry. Mercury forms two chlorids, $HgCl_2$, corrosive sublimate, "bichlorid," and $HgCl$, mercurous chlorid, calomel. Both sublime readily, mercuric chlorid fusing before sublimation. Mercurous chlorid is insoluble in water and is largely used as a medicine. Mercuric chlorid is sparingly soluble in water; more soluble in ammonium chlorid; soluble also in alcohol and ether. This last is unusual for salts. It is a powerful germicide, and used in medicine, especially as an antiseptic.

Mercury forms two iodin salts, HgI (yellow) and HgI_2 (red). Mercuric iodid (HgI_2) is insoluble in water but easily soluble in a solution of potassium iodid, forming $HgI_2.2KI$. It is a stronger germicide than mercuric chlorid. Both iodids are used in medicine.

Experiment 99.—To a few drops of mercurous nitrate ($HgNO_3$) solution add hydrochloric acid. Test with ammonium hydroxid.

Experiment 100. — To a few drops of mercurous nitrate ($HgNO_3$) solution add potassium iodid (KI); add potassium iodid to solution of mercuric nitrate ($Hg(NO_3)_2$); in the latter case add an excess of potassium iodid.

Experiment 101.—Heat in a closed tube a small drop of mercury with a little iodin. Write the reaction.

THE HALIDS OF GROUP III

242. Properties.—Boron chlorid (BCl_3) is a colorless liquid which is decomposed by water with the formation of hydrochloric acid and boric acid.

$$BCl_3 + 3HOH = 3HCl + B(OH)_3.$$
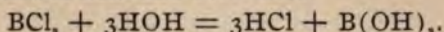
Aluminum chlorid ($AlCl_3$) is a white, crystalline solid which is very deliquescent. It forms double chlorids with the alkaline chlorids and was once used in the preparation of aluminum. It is used to promote reactions between organic bodies. When a solution of aluminum chlorid in water is evaporated, it is decomposed with the formation of hydrochloric acid and aluminum hydroxid.

$$AlCl_3 + 3HOH = 3HCl + Al(OH)_3.$$
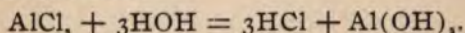
This reaction is general in the case of many of the halids of the less positive elements.

The other members of this group form chlorids of the generic formula MCl_3, which are soluble in water without decomposition. Thallium also forms a chlorid, thallous chlorid ($TlCl$), which is insoluble in water.

THE HALIDS OF GROUP IV

243. Properties.—Carbon will not unite directly with the halogens, but several compounds may be formed by the action of the halogens upon hydrocarbons; *e. g.*,

$$CH_4 + 4Cl_2 = 4HCl + CCl_4.$$
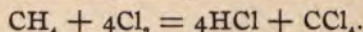
The halogen compounds of carbon are insoluble liquids in the case of chlorids, solids in the case of bromids and iodids. Carbon tetrachlorid is decomposed by water at 200°.

$$CCl_4 + 2H_2O = 4HCl + CO_2.$$
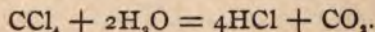
Silicon tetrachlorid ($SiCl_4$) is formed by the action of chlorin on amorphous silicon ; or on a mixture of silica and carbon ; or on magnesium silicid (Mg_2Si). It is a strongly fuming liquid which is instantly decomposed by water.

$$SiCl_4 + 4HOH = Si(OH)_4 + 4HCl.$$
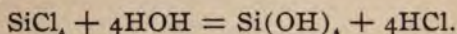
Silicon tetrafluorid (SiF_4) is formed when hydrofluoric acid acts on silica (*e. g.*, sand).

$$4HF + SiO_2 = 2H_2O + SiF_4.$$
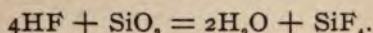
Silicon tetrafluorid is a colorless gas, fuming in moist air. It is at once decomposed by water.

$$SiF_4 + 4HOH = Si(OH)_4 + 4HF.$$
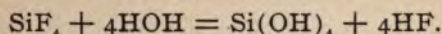
The gelatinous $Si(OH)_4$, silicic acid, is precipitated and the hydrofluoric acid formed unites with more of the silicon tetrafluorid forming $SiF_4.2HF$ or H_2SiF_6, fluorsilicic acid, an unstable acid, which however forms a series of stable salts known as fluorsilicates.

Titanium forms a chlorid ($TiCl_4$) which is a liquid and can be boiled without change. It is decomposed by water forming oxychlorids. Zirconium gives a very similar chlorid and oxychlorids.

Tin dissolves in hydrochloric acid with evolution of hydrogen and formation of stann*ous* chlorid ($SnCl_2$). When chlorin acts on tin the stann*ic* chlorid ($SnCl_4$) is formed. When a solution of stannous chlorid is treated with chlorin or some other oxidizing substance as potassium chlorate, a solution of stannic chlorid is formed. Stannous chlorid is a white solid, soluble in water, but soon decomposing into a stannous oxychlorid and hydrochloric acid. Stannous chlorid is a strong reducing agent. Stannic chlorid is a fuming liquid which forms with three molecules of water a white, crystalline solid,

soluble in water, but decomposing by heat or long standing at ordinary temperatures into hydrochloric acid and stannic hydroxid or stannic acid, $SnO(OH)_2$.

$$SnCl_4 + 4HOH = SnO(OH)_2 + 4HCl + H_2O.$$
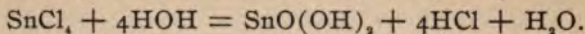
This reaction is analogous to the reaction of many of the chlorids of negative and weakly positive elements.

Experiment 102.—Reduce each of the following solutions with a solution of stannous chlorid ($SnCl_2$); potassium permanganate ($KMnO_4$); potassium chromate (K_2CrO_4); and mercuric chlorid ($HgCl_2$).

Lead chlorid is formed by the action of hydrochloric acid or a soluble chlorid on any soluble lead salt; lead chlorid, being only slightly soluble, is precipitated. Lead chlorid is however soluble in hot water or a large quantity of cold water. Lead tetrachlorid ($PbCl_4$) is formed when lead dioxid is dissolved in very cold hydrochloric acid, but is very unstable, heat decomposing it, even in solution in the acid, to lead chlorid and chlorin, while water decomposes it into lead oxid and hydrochloric acid.

Lead iodid (PbI_2) is formed similarly to lead chlorid, but is less soluble in water. It is bright yellow and crystallizes out from its solution in hot water in golden scales.

Experiment 103.—Precipitate a solution of lead acetate ($Pb(C_2H_3O_2)_2$) with hydrochloric acid; warm until the precipitate has dissolved and then set away to cool.

Experiment 104.—Repeat the last experiment using potassium iodid in place of hydrochloric acid. (It may be necessary to add (distilled) water to effect complete solution.) Write formulas for both reactions.

THE HALIDS OF GROUP V

244. Properties.—The halogen compounds with nitro-

gen are among the most unstable bodies known. When iodin (dissolved in alcohol) acts upon a solution of ammonia, a grayish black precipitate of nitrogen iodid (NI_3) is thrown down. Nitrogen iodid may be filtered off and dried. When dry the slightest touch will suffice to explode it. Even when moist it rapidly decomposes. Nitrogen chlorid is a heavy yellow oil, and even more explosive than nitrogen iodid.

Phosphorus, arsenic, antimony, and bismuth all unite directly with chlorin to form chlorids. In each case the trichlorid is formed (PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$), but in case an excess of chlorin is present with phosphorus and antimony a pentachlorid is formed, (PCl_5 and $SbCl_5$). Phosphorus and arsenic trichlorids are liquids, antimony and bismuth trichlorids are solids, and from their soft consistency and easy fusibility were known to the alchemists as butter of antimony and butter of bismuth, respectively.

Phosphorus pentachlorid is a solid (white). Antimony pentachlorid is a liquid.

245. Decompositions with Water.—All of these chlorids are decomposed by water ; thus :

$$PCl_3 + H_2O = P\begin{matrix} \diagup O \\ \diagdown Cl \end{matrix} \text{ (phosphorus oxychlorid)} + 2HCl.$$

$$AsCl_3 + H_2O = As\begin{matrix} \diagup O \\ \diagdown Cl \end{matrix} \text{ (arsenious oxychlorid)} + 2HCl.$$

$$SbCl_3 + H_2O = {}^1Sb\begin{matrix} \diagup O \\ \diagdown Cl \end{matrix} \text{ (antimony oxychlorid)} + 2HCl.$$

$$BiCl_3 + H_2O = Bi\begin{matrix} \diagup Cl \\ \diagdown O \end{matrix} \text{ (bismuth oxychlorid)} + 2HCl.$$

---
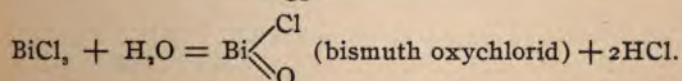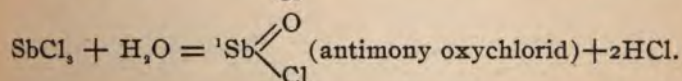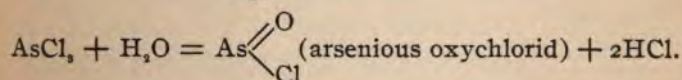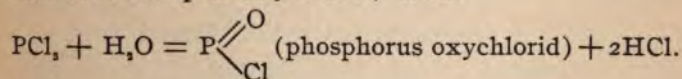
[1] With antimony a more complex oxychlorid than $Sb\begin{matrix} \diagup O \\ \diagdown Cl \end{matrix}$ is generally formed.

Phosphorus trichlorid and pentachlorid and phosphorus oxychlorid ($\overset{v}{P}OCl_3$), when an excess of water is present, are completely decomposed ; *viz.*,

$$PCl_3 + 3H_2O = P\overset{\displaystyle OH}{\underset{\displaystyle OH}{-OH}}, \text{ (phosphorous acid) } + 3HCl.$$

$$P\overset{\displaystyle O}{\underset{\displaystyle Cl_3}{\big\langle}} + 3H_2O = OP(OH)_3 \text{(phosphoric acid)} + 3HCl.$$

$$PCl_5 + 4H_2O = OP(OH)_3 \text{ (phosphoric acid) } + 5HCl.$$
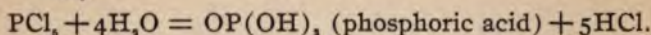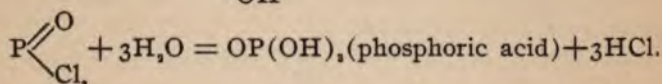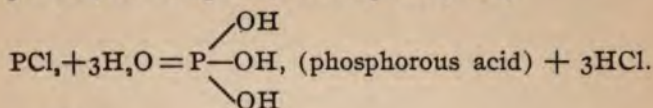
By the presence of a large amount of free hydrochloric acid, the oxychlorids of arsenic, antimony, and bismuth can be kept in solution in water, while the presence of tartaric acid prevents antimony trichlorid from precipitating when water is added.

Experiment 105.—Add a few drops of antimony trichlorid ($SbCl_3$) to a test-tube partly filled with water. What is the precipitate ? Divide the precipitate in two parts ; dissolve one part in concentrated hydrochloric acid, the other in tartaric acid.

THE HALIDS OF GROUP VI

246. Properties.—The halogen compounds of oxygen are unstable and will be considered under oxygen compounds later. With sulphur, selenium, and tellurium, the halogens unite directly.

When chlorin is led into melted sulphur, S_2Cl_2 is formed, a heavy, yellowish red liquid. Its formula may be $Cl—\overset{ii}{S}—\overset{ii}{S}—Cl$ or possibly $S=\overset{iv}{S}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{\big\langle}}$. It is a solvent for sulphur, and this solution is used in vulcanizing rubber.

When chlorin is led into S_2Cl_2 at low temperatures (6° to 8°), SCl_2 is formed, $S{<}^{Cl}_{Cl}$; when chlorin is led into this at —20°, the tetrachlorid, SCl_4, is formed. SCl_2 and SCl_4 are both liquid.

With the members of the Positive Series, Group VI, chlorin unites directly. Several compounds are formed with each element; *viz.*, $CrCl_2$, $CrCl_3$; $MoCl_3$, $MoCl_4$, $MoCl_5$; WCl_2, WCl_4, WCl_5, WCl_6 ; $UrCl_3$, $UrCl_4$, $UrCl_5$.

THE HALIDS OF GROUP VII

247. Properties.—The halogens form several compounds with each other by direct union ; *viz.*, ClBr, ClI and Cl_3I, and BrI. All are unstable compounds.

With manganese the halogens form compounds in which manganese is bivalent, $MnCl_2$, etc. Manganese is in many respects so strongly positive that in its ordinary relations it resembles greatly the elements of Group II, Negative Series, acting like them as a bivalent element. Its salts are similarly formed and are very much like them ; indeed they are in many instances isomorphous with those of zinc.

THE HALIDS OF GROUP VIII

248. Properties.—What has been said of manganese regarding its resemblance to the elements of Group II, is also true of iron, cobalt, and nickel. With the halogens, nickel and cobalt act only as bivalent elements, $NiCl_2$ (green), $CoCl_2$ (rose). Iron acts as bivalent in ferrous chlorid ($FeCl_2$) and as trivalent in ferric chlorid ($FeCl_3$). These compounds may be formed by the direct

action of chlorin on the metal or by solution of the metal or some of its compounds in hydrochloric acid.

If iron is dissolved in hydrochloric acid, ferrous chlorid is formed.

$$Fe + 2HCl = FeCl_2 + H_2.$$
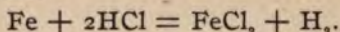
If chlorin acts on iron, ferric chlorid is formed.

$$2Fe + 3Cl_2 = 2FeCl_3.$$
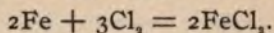
Ferric chlorid is also formed when ferric compounds are dissolved in hydrochloric acid,

$$Fe_2O_3 + 6HCl = 3H_2O + 2FeCl_3,$$
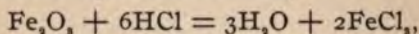
or when ferrous chlorid is oxidized by chlorin, nitric acid (in presence of hydrochloric acid), etc. Ferrous chlorid on standing tends to become oxidized to a ferric compound.

The other elements of Group VIII form several types of chlorids. All form chlorids in which they act as bivalent, $RuCl_2$(?), $OsCl_2$, $RhCl_2$ $IrCl_2$; $PdCl_2$, $PtCl_2$; all but palladium and platinum form trichlorids, $RuCl_3$, $OsCl_3$ $RhCl_3$, $IrCl_3$; while all but rubidium and rhodium form tetrachlorids, $OsCl_4$ $IrCl_4$, $PdCl_4$, $PtCl_4$. The chlorids in italics may be considered as the most important formed by each metal.

When oxidized by nitric acid, $RuCl_3$ forms $RuCl_3NO$, and not $RuCl_4$.

PART V

OXIDS AND SULPHIDS

Binary Compounds of the Elements of Group VI and their Derivatives

249. Nature of the Oxids.—Under this heading will be considered the binary compounds of oxygen and sulphur with the more positive elements and the derivatives of these compounds. The compounds of selenium and tellurium have been little studied but seem to resemble the compounds of sulphur. The members of the positive series of this group form no binary compounds with the positive elements, but do give them with the negative elements.

Oxygen forms compounds, called oxids, with all the elements except fluorin, though the oxids of bromin have not been obtained in a pure state. With a number of the elements, oxygen forms more than one oxid.

In Part III we have seen that hydrogen combines most readily with the more negative elements and has little tendency to combine with the more positive elements. With oxygen, as with the halogens, the gradation of affinity is in the opposite direction, the most positive elements having the greatest affinity for oxygen and holding it most firmly. The affinity of oxygen for the more negative elements seems to be stronger than that of the halogens. The oxids of the positive elements are insoluble in water, except those of the alkalies.

The negative oxids are generally quite soluble in water. Closely related to the oxids is a class of compounds containing both oxygen and hydrogen, called hydroxids.

250. Methods of Formation.—Oxids may be formed :

1. By heating (a) elements or (b) compounds in oxygen or air :

$$Cu + O = CuO.$$
$$2ZnS + 3O_2 = 2ZnO + 2SO_2.$$
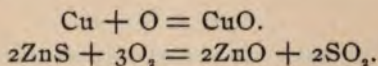
2. By heating hydroxids or certain salts.

$$Cu(OH)_2 = H_2O + CuO.$$
$$CaCO_3 = CO_2 + CaO.$$
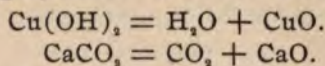
Hydroxids may be formed :

1. By adding water to oxids.

$$P_2O_5 + 3H_2O = 2PO(OH)_3.$$
$$CaO + H_2O = Ca(OH)_2.$$
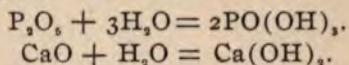
2. By decomposing water by means of very positive elements.

$$2Na + 2H_2O = 2NaOH + H_2.$$
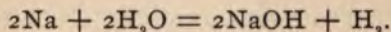
3. By double decomposition, when the hydroxid sought is insoluble ; *e. g.*,

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl.$$
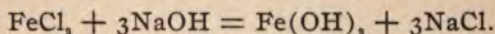
Experiment 106.—*a.* Heat a piece of copper foil in the oxidizing flame of the Bunsen burner. *b.* Heat zinc blende (ZnS) on charcoal before the oxidizing flame of the blowpipe. Notice the incrustation of zinc oxid (ZnO) and odor of sulphur dioxid (SO_2).

Experiment 107.—*a.* Add a small piece of lime (CaO) to water. Test the solution for calcium hydroxid ($Ca(OH)_2$). *b.* Place a bit of sodium in water in a porcelain dish. Test the solution for sodium hydroxid. *c.* Add sodium hydroxid solution to a solution of ferric chlorid ($FeCl_3$).

251. Chemical Character.—We may premise the con-

sideration of the oxids by noting that they have very different properties according as they are oxids of positive or negative elements. Oxids of the more negative elements unite with water to form acids; oxids of the more positive elements unite with water to form bases. The general properties of acids and bases have already been given. Their most important chemical property is that they may unite with one another with the elimination of water, neutralizing each other and forming salts; for example : Acid-forming oxid,

$$SO_3 + H_2O = H_2SO_4. \quad \text{Sulphuric acid.}$$

Base-forming oxid,

$$Na_2O + H_2O = 2NaOH. \quad \text{Sodium hydroxid.}$$

A salt,

$$H_2SO_4 + 2NaOH = 2H_2O + Na_2SO_4. \quad \text{Sodium sulphate.}$$
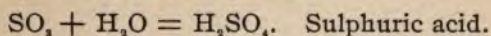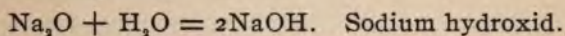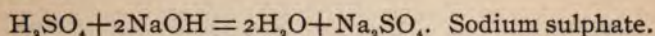
Certain of the less positive and less negative elements form oxids which act as acids toward strong bases, and bases toward strong acids; for example :

$$SnO_2 + H_2O = SnO(OH)_2 ;$$
$$SnO(OH)_2 + 2H_2SO_4 = 3H_2O + Sn(SO_4)_2 ;$$
$$\text{or } SnO_2 + H_2O = H_2SnO_3 ;$$
$$H_2SnO_3 + 2NaOH = 2H_2O + Na_2SnO_3.$$
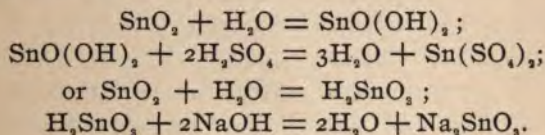
252. The Sulphids.— The compounds of sulphur, known as sulphids, resemble those of oxygen. The affinity of sulphur for both the positive and the negative elements is less strong than that of oxygen, and its compounds less stable and generally less numerous.

All the sulphids except those of the alkalies and alkaline earths are insoluble. The sulphids of many of the positive elements are found in nature; indeed this is the most abundant mode of occurrence of many elements.

The most common ores of the metals are oxids and sulphids.

253. Formation of Sulphids.—The sulphids of a large number of the elements can be formed by direct union with sulphur.

$$Fe + S = FeS.$$
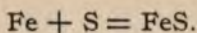
Many sulphids of positive elements may be formed by the action of hydrogen sulphid, or soluble sulphids, upon solutions of their salts.

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$
$$FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4.$$
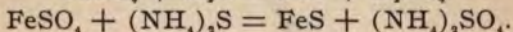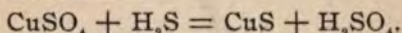
Analogous to the hydroxids are the hydrosulphids (sulphydrates) which may be looked upon as sulphids united with hydrogen sulphid.

$$CaO + H_2O = Ca(OH)_2.$$
$$CaS + H_2S = Ca(SH)_2.$$
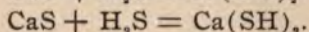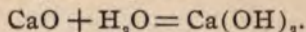
Like oxids, sulphids may be base-forming or acid-forming. The hydrosulphids of the strongly positive elements are bases; of these only the hydrosulphids of the alkalies and alkaline earths are known. The hydrosulphids of the negative elements are acids; but here again very few are known in the free state, though salts of quite a number of them, called thio-acids, are known.

Experiment 108.—Treat with hydrogen sulphid (H_2S) and also with ammonium sulphid (($NH_4)_2S$) the following salts dissolved in water: $Pb(NO_3)_2$, $CuSO_4$, $SnCl_2$, $SnCl_4$, $FeCl_3$, $KCr(SO_4)_2$, or $Cr_2(SO_4)_3$, $ZnSO_4$, $MgSO_4$. What is formed in each case?

THE OXIDS OF GROUP I

254. General Characteristics.—The typical formula is M_2O, where M represents any of the elements of the

group, but there may be several other oxids. These are, in general, formed by burning the metal in the air or in oxygen. They combine with great readiness with water, forming the hydroxids, and are commonly made use of in this form. In the second or negative series these hydroxids are not formed by direct union with water and are not very stable. With the exception of these the hydroxids are deliquescent, very soluble bodies, strong bases, and strongly caustic.

They have an alkaline taste and act with great energy upon acids. They are stable even when heated to a high temperature. The hydroxids are used in the place of the oxids because they are more easily handled and prepared.

Lithium Oxid, Li_2O

255. Preparation and Properties.—Lithium oxidizes slowly in oxygen at ordinary temperatures. When heated, the lithium takes fire and gives a white oxid. It can be prepared also by heating lithium nitrate. A white crystalline mass is obtained which dissolves slowly in water forming the hydroxid ($LiOH$). This hydroxid is white, cauterizes organic matter, and absorbs carbon dioxid from the air. It combines readily with acids forming lithium salts. The lithium salts are too rare and costly for extensive use; the most important are the carbonate and the chlorid.

Sodium Monoxid, Na_2O

256. Preparation and Properties.—Sodium forms two oxids. The first, sodium monoxid, Na_2O, is the typical oxid of the group. On heating the metal in the air this oxid and the dioxid are both formed together.

It is best prepared by heating the hydroxid and the metal together.

$$NaOH + Na = Na_2O + H.$$
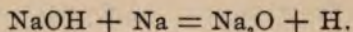
It is a grayish white mass, melting at a red heat. When brought in contact with water there is a violent action, much heat is evolved, and sodium hydroxid is formed.

Sodium hydroxid (NaOH) is generally formed by treating a solution of sodium carbonate with slaked lime. The calcium carbonate being insoluble settles to the bottom and the clear liquid containing the sodium hydroxid is drawn off and evaporated.

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$
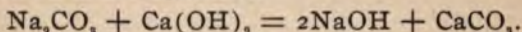
This gives the caustic soda of commerce. It is a white solid which readily absorbs moisture from the air. It can be melted without decomposition but suffers decomposition at a very high temperature. It is a most valuable substance and is used in many industries. It is used in the manufacture of soaps because of its action upon fats, and also in the decomposition of silicates and where silica is to be removed.

Sodium Dioxid, Na_2O_2

257. Properties.—This is formed when sodium is heated in oxygen. It is a white deliquescent substance, which absorbs carbon dioxid. When water is added to it the dioxid is decomposed with evolution of heat and formation of oxygen and the hydroxid. It explodes when brought in contact with a combustible substance and a little water, and hence has to be handled with care. The oxygen liberated from it can be used in bleaching. This dioxid is manufactured on a considerable scale for oxidizing and bleaching purposes. There seem to be other

oxids of sodium, as Na_4O, but little is known about them.

Sodium furnishes a very large list of useful salts. The most important are the carbonate, chlorid, nitrate, and sulphate.

Potassium Monoxid, K_2O

258. Preparation and Properties.—Potassium forms two oxids. When potassium is burned in the air both oxids are first formed; on further heating, the mixture evolves oxygen, leaving a residue of the monoxid. The same oxid is formed by heating potassium hydroxid with metallic potassium. The reaction is the same as in the case of sodium hydroxid. Potassium monoxid is a gray, brittle mass, which combines energetically with water, and may become red hot when moistened. This union with water gives potassium hydroxid.

Potassium hydroxid (KOH) is known as caustic potash and is prepared in the same way as sodium hydroxid. It is deliquescent, very soluble in water, and melts, volatilizes, and is decomposed at higher temperatures than sodium hydroxid. It absorbs carbon dioxid from the air, changing into the carbonate as do lithium and sodium hydroxids. It has an alkaline taste and a slight peculiar odor. With acids it combines to form salts. Its industrial use is limited as it can be substituted by the cheaper sodium hydroxid.

Potassium Tetroxid, K_2O_4

259. Preparation and Properties.—This is prepared by heating potassium in oxygen and is a dark yellow powder. The properties are similar to those of sodium dioxid.

The compounds of potassium are very numerous and

useful. They are formed after the type of the monoxid, K_2O. The carbonate, sulphate, nitrate, chlorid, and silicate are among the most important.

OTHER OXIDS OF GROUP I

Rubidium and cesium probably form oxids and hydroxids analogous to those of potassium, but on account of the rarity of the elements these compounds have been little studied.

Ammonium hydroxid is supposed to be formed when ammonia is dissolved in water. It has never been separated from the solution nor prepared in a pure form. The solution in water gives off ammonia at ordinary temperatures and is easily decomposed by heating. It is strongly basic and in its chemical behavior resembles potassium hydroxid. With acids it gives ammonium salts.

Experiment 109.—Form sodium hydroxid (NaOH): (*a*) by the action of sodium on a small quantity of water; (*b*) by adding lime (CaO) to a solution of sodium carbonate (Na_2CO_3) until a little of the clear solution ceases to effervesce with an acid, and filtering. Evaporate both solutions and compare the residues. Redissolve each in water, and compare their action on solutions of copper sulphate ($CuSO_4$), zinc sulphate ($ZnSO_4$), mercurous nitrate ($HgNO_3$) and mercuric nitrate ($Hg(NO_3)_2$). (See following sections for the reactions.)

THE SULPHIDS OF GROUP I

As these are similar for the different metals, the sulphids of sodium and ammonium alone will be considered.

Sodium Sulphid, Na_2S

260. Preparation and Properties.—When hydrogen

sulphid is led into a solution of sodium hydroxid, sodium hydrosulphid is formed.

$$NaOH + H_2S = H_2O + NaSH.$$
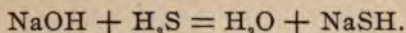
If now a further (equal) quantity of sodium hydroxid be added to this, sodium sulphid is formed.

$$NaSH + NaOH = Na_2S + H_2O.$$
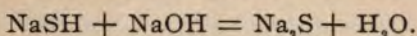
Sodium sulphid is also formed by the action of carbon on sodium sulphate at high temperatures (as in the second stage of the Le Blanc process of making soda).

$$Na_2SO_4 + 4C = 4CO + Na_2S.$$
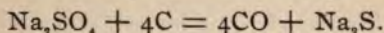
It is also formed, together with higher sulphids, when any sulphur compound is fused on charcoal with sodium carbonate.

Sodium sulphid is a colorless or slightly colored solid, very soluble in water, the solution, colorless at first, soon becoming yellow from decomposition and the formation of higher sulphids. From the solution, sodium sulphid crystallizes with water of crystallization. It is used as a laboratory reagent, but is generally replaced by ammonium sulphid.

Higher sulphids are known, as Na_2S_2 (analogous to Na_2O_2) Na_2S_3, Na_2S_4, and Na_2S_5, formed by the solution of sulphur in any of the lower sulphids.

Sodium Hydrosulphid, NaSH

261. Preparation and Properties.—When hydrogen sulphid is led into a solution of sodium sulphid, the hydrosulphid is formed.

$$Na_2S + H_2S = 2NaSH.$$

This is analogous to the reaction

$$Na_2O + H_2O = 2NaOH.$$
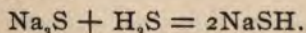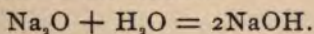
Potassium hydrosulphid may also be formed by heating potassium in a stream of hydrogen sulphid.

$$2K + 2H_2S = 2KSH + H_2.$$

This is analogous to the reaction

$$2K + 2H_2O = 2KOH + H_2.$$
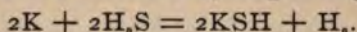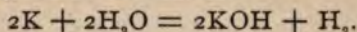
Ammonium Sulphid, $(NH_4)_2S$

262. Preparation and Properties.—Ammonium sulphid is formed, as above, by leading hydrogen sulphid into ammonium hydroxid until it is saturated, and then adding an equal quantity of ammonium hydroxid:

$a.$ $NH_4OH + H_2S = NH_4SH + H_2O.$
$b.$ $NH_4SH + NH_4OH = (NH_4)_2S + H_2O.$
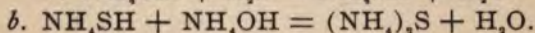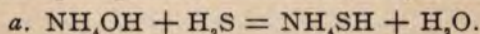
On adding sulphur it is dissolved and higher sulphids are formed, chiefly $(NH_4)_2S_5$. Ammonium pentasulphid is known in the laboratory as yellow ammonium sulphid.

Both of the sulphids of ammonium are used as important laboratory reagents.

OXIDS OF THE NEGATIVE SERIES OF GROUP I.

263. Copper Oxids.—Copper forms two principal oxids, cuprous oxid (Cu_2O) and cupric oxid (CuO). Both of these oxids are base-forming and from them are derived the two classes of copper salts.

Cuprous Oxid, Cu_2O

264. Preparation.—This is found as one of the ores of copper. It is called cuprite or red copper ore. It is formed on heating copper in an insufficient amount of air; thus it is seen on the inside of scales from heated

pieces of copper. It is generally prepared by reduction from the higher oxid of copper; that is, by removing a part of the oxygen from it. This may be done by boiling a solution of copper sulphate with an alkaline hydroxid and glucose. The alkaline hydroxid, as will be seen, gives first cupric hydroxid, which is reduced by the glucose.

265. Properties.—Cuprous oxid is a red powder, insoluble in water. The dry oxid is stable but when moist it slowly absorbs oxygen from the air and becomes cupric oxid. It colors glass red and is sometimes used for that purpose.

Cuprous hydroxid (CuOH) is obtained by precipitating a cuprous compound with an alkaline hydroxid.

$$CuCl + NaOH = CuOH + NaCl.$$
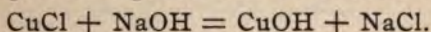
It is a yellow powder, easily absorbing oxygen from the air and becoming blue, changing into the higher hydroxid, $Cu(OH)_2$. It is decomposed by heating. There is a class of copper salts formed after the type of this oxid and hydroxid. They are called cuprous salts. Some are unstable and they are less important than the salts formed from the cupric oxid.

Cupric Oxid, CuO

266. Preparation.—This oxid occurs as black copper ore but is not so abundant an ore as the red copper ore. It can be prepared by heating the nitrate, carbonate, or hydroxid. More commonly it is obtained by heating the metal in air or in oxygen. When the scales from heated copper are observed, the inside is found to be red from the formation of cuprous oxid and the outside black from the cupric oxid.

267. Properties.—Cupric oxid is a black solid, insoluble

in water. It is stable even at high temperatures but loses its oxygen on being heated with reducing substances. It colors glass green. Dissolved in acids it gives cupric salts.

268. Cupric Hydroxid, $Cu(OH)_2$.—This can be prepared by precipitating a solution of a cupric salt with an alkaline hydroxid.

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4.$$
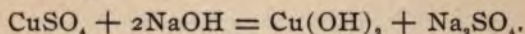
It is a light blue solid, insoluble in water. On boiling the freshly precipitated hydroxid, it loses water and is partly changed into the oxid.

$$Cu(OH)_2 = CuO + H_2O.$$
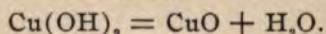
It is a general principle that when any substance containing hydrogen and oxygen is heated, water will be formed. Thus most hydroxids will be converted into oxids. Elements weak in chemical affinity cannot hold the hydroxyl groups as firmly as more active elements. Thus the hydroxid of copper begins to decompose below 100° and in the presence of water.

When certain organic substances are present in a copper solution, the hydroxid precipitated by sodium hydroxid is readily soluble in an excess of the reagent, forming an azure blue solution. (Tartrates, glycerol, and sugars act in this way.) If now a reducing substance, as grape-sugar, be added and the solution heated, cuprous oxid (Cu_2O) is precipitated as a fine red or orange powder. Blue cupric hydroxid, when heated in an alkaline solution with a reducing agent, loses both water and oxygen forming cuprous hydroxid.

$$Cu\begin{matrix} OH \\ OH \end{matrix} \Big\rangle + \left(\begin{smallmatrix} \text{oxidizable} \\ \text{substance} \end{smallmatrix}\right) = \begin{matrix} Cu \\ Cu \end{matrix}\Big\rangle O + 2HOH + \left(\begin{smallmatrix} \text{oxidizable} \\ \text{substance} \end{smallmatrix} + O\right).$$
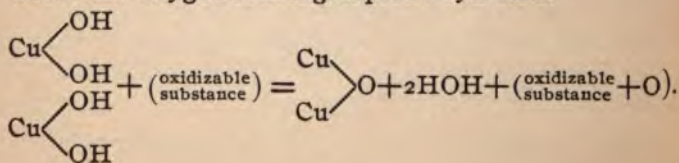
Arsenious salts cause this reaction :

$$2Cu(OH)_2 + Na_3AsO_3 = Cu_2O + H_2O + Na_3AsO_4.$$
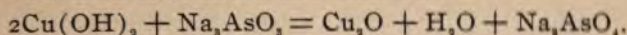
The dried precipitate does not decompose so easily. The freshly precipitated hydroxid is soluble in ammonia to a deep azure blue solution. This solution has the power of dissolving cellulose. The hydroxid is easily dissolved by acids, giving cupric salts. The most important of these are the sulphate or bluestone, nitrate, the basic acetate, and basic carbonate.

269. Classes of Copper Compounds.—Thus there are two classes of salts of copper, *cuprous* and *cupric*. Wherever an element gives two such classes the one with the smallest proportion of negative element or group is distinguished by the termination *-ous* and the higher oxid, or one with the greater proportion, by the termination *-ic*. It is easy to change from one of these classes to the other. The change from the lower to the higher (*-ous* to *-ic*) is called oxidation, and the reverse change reduction. In these two classes of salts, copper acts as differently, as if it were two distinct elements. Indeed in some of the classifications of the elements, copper in these two states is placed under different groups. Copper in the cuprous compounds is analogous to the type and other members of the first group. It is univalent. In the cupric salts it is bivalent and more like elements of the second group. Thus the oxids would be written $Cu''=O$ and $Cu'-O-Cu'$; the chlorides $Cu'' \diagup{\!\!\!Cl} \diagdown{\!\!\!Cl}$ and $Cu'-Cl$.
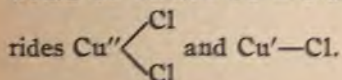
Experiment 110.—Compare the four following reactions :

1. $CuSO_4 + NaOH$.
2. $CuSO_4 + NaOH + $ heat.
3. $CuSO_4 + $ glycerin $ + NaOH$ (excess) $ + $ heat.
4. $CuSO_4 + $ glycerin $ + NaOH + $ grape-sugar $ + $ heat. What is formed in each case? Write equations.

Silver Oxid, Argentic Oxid, Ag_2O

270. Preparation and Properties.—This is the typical and the chief oxid of silver though two others are known. It is prepared by precipitation from a solution of silver nitrate by means of an alkaline hydroxid. Ordinarily this would give a hydroxid but the hydroxid of silver does not exist at common temperatures. The moist oxid acts in many ways as a hydroxid, however. The hydroxid is then more unstable than cupric hydroxid and is decomposed into silver oxid and water at $-40°$. The oxid prepared in this way forms an almost black powder, insoluble in water and having an alkaline reaction. It absorbs carbon dioxid from the air. It is decomposed by heating to a temperature of $250°$ and gives up its oxygen easily to oxidizable substances. Silver cannot be oxidized directly by means of oxygen even at high temperatures, though it absorbs oxygen when melted, but gives it off again when cooled. Ozone oxidizes it directly.

271. Other Oxids of Silver.—Argentous oxid, Ag_4O, may be formed by reduction from silver salts. There is some question as to its existence and it seems incapable of giving any salts.

Silver dioxid, Ag_2O_2, is formed by the action of ozone upon silver.

Silver salts are formed on the type of the first oxid, Ag_2O, which is analogous to the type, sodium. In these

salts silver is univalent. The most important salts are the nitrate, chlorid, bromid, and cyanid.

Gold Monoxid, Aurous Oxid, Au_2O

272. Preparation and Properties.—Gold forms two oxids, aurous oxid, Au_2O, and auric oxid, Au_2O_3. Aurous oxid, as indeed both of the oxids of gold, must be prepared indirectly. It is obtained by adding cold dilute potassium hydroxid to aurous chlorid. It is a violet-colored powder which is decomposed at 250°. It is not much acted upon by acids but is decomposed by alkalies.

Gold Trioxid, Auric Oxid, Au_2O_3

273. Preparation and Properties.—This oxid is obtained by heating the hydroxid to 100°. It is easily decomposed by further heating. It is a dark, insoluble powder. Gold hydroxid, $Au(OH)_3$, is best prepared by heating a solution of gold trichlorid with an excess of magnesia. If prepared by an alkaline hydroxid, some of the alkali is always retained. It is a brown powder, decomposing in the light or on heating to 100°. It is a weak base, forming salts, called auric salts, with strong acids and combining with strong bases giving salts called aurates in which the gold hydroxid plays the part of an acid. From this it will be seen that whether a body acts as an acid or base depends sometimes upon its electrochemical relation to the substance with which it is brought in contact.

Gold forms two classes of salts, aurous and auric. In the former it is univalent, in the latter trivalent. Gold cannot be oxidized directly either by oxygen or ozone. Its most important compound is the auric chlorid, $AuCl_3$.

By the action of ammonia upon moist silver oxid or upon gold hydroxid, peculiar compounds are obtained, called respectively fulminating silver and fulminating gold, both of which are explosive.

SULPHIDS OF THE NEGATIVE SERIES OF GROUP I

The sulphids of copper, silver, and gold are closely analogous to the oxids, and several of them occur in nature as copper glance (Cu_2S), blue copper (CuS), and silver glance (Ag_2S). The double sulphid of copper and iron, chalcopyrite (Cu_2S,Fe_2S_3), is one of the most important ores of copper.

THE OXIDS OF GROUP II

274. General Characteristics.—The typical form of the oxid here is MO. They are generally white insoluble bodies absorbing carbon dioxid from the air. The hydroxids are formed by direct union with water or in the case of the Negative Series by precipitation.

The oxids themselves may be obtained by burning the metals. As this method is not generally practicable on account of the cost of the metals, the oxids are obtained by heating the carbonates, nitrates, or other compounds containing volatile acids. The oxids of the group element, type, and Positive Series are basic and those of greater atomic weight are caustic but less so than the oxids of the alkalies.

These oxids are known as the *alkaline earths*, though the name is more strictly applied solely to calcium, strontium, and barium oxids. The three oxids above mentioned, when dissolved in water, impart to it an alkaline reaction, and hence the name of *alkaline earths*. These oxids do not occur in nature, but a very impure oxid of

magnesium and the hydroxid of magnesium, $Mg(OH)_2$, do occur in nature.

The elements of this group are bivalent in their typical oxids. One element of the Negative Series, mercury, forms two classes of salts. The oxids of this group absorb carbon dioxid on exposure to it and become carbonates.

Glucina, GlO

275. Preparation and Properties.—Glucinum forms only one oxid, glucina, GlO. This can be prepared by burning the metal or by heating the hydroxid, nitrate, etc. It is a white powder, very stable, insoluble in water, and soluble in strong acids forming salts of glucinum.

Glucinum hydroxid $Ge(OH)_2$, is precipitated from a solution of a glucinum salt by ammonium hydroxid. It is a white powder, easily soluble in acids and alkalies and is changed into the oxid on ignition. In the mode of formation and properties of this hydroxid, glucinum shows analogies to the elements of Group III.

Magnesium Oxid, MgO

276. Preparation and Properties.—Magnesium forms but one oxid, magnesia, MgO. This is generally made by heating the carbonate. Any of the methods mentioned above would give the oxid. From the mode of preparation it was called *magnesia usta* or calcined magnesia. It is a very light, white, powder, insoluble, tasteless, faintly alkaline towards litmus, and melting without decomposition. It slakes slowly in water, forming the hydroxid.

Magnesium hydroxid, $Mg(OH)_2$, can also be obtained by precipitation with an alkaline hydroxid. It is

a white powder which is changed into the oxid on heating. The oxid is used in medicine; also for crucible lining in the making of basic steel.

Only one class of magnesium salts is known. These are formed on the type of oxid MgO. In them magnesium is bivalent. There are a large number of these salts known and many of them are very useful. The chief compounds are the carbonate, sulphate, chlorid, phosphate, and silicate.

Calcium Oxid, Lime, CaO

277. Preparation and Properties.—Calcium forms two oxids, lime CaO and calcium dioxid CaO_2.

Lime is obtained by heating some form of the carbonate, as marble or limestone. This is a large industry and is carried out in lime-kilns.

$$CaCO_3 = CaO + CO_2.$$
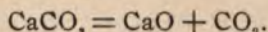
Lime forms a white mass which does not melt nor is it decomposed on heating, but it becomes intensely incandescent. On this account it is used in the Drummond or lime-light. It absorbs water and carbon dioxid from the air. Placed in water it combines with it with great energy, forming the hydroxid. The action generates a great deal of heat and is called slaking. The resulting hydroxid is called slaked lime. The oxid is a strong caustic; the hydroxid is more mildly caustic.

$$CaO + H_2O = Ca(OH)_2.$$
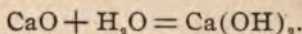
Calcium hydroxid is a dry white powder. It is somewhat soluble in water and the solution is known as limewater. When merely stirred up with a little water it is called milk of lime. It has a strong alkaline reaction to litmus and combines readily with acids giving salts of calcium.

Lime is extensively used in mortar. Here the lime is slaked and made into a cream with water. Sand is then mixed with it so that each grain of sand shall have a coating of calcium hydroxid around it. As the sand is the strength of the mortar, it is desirable that the layer or coating of calcium hydroxid, the binding material, shall be as thin as possible. Sharp sand makes better mortar than that with rounded grains. The hardening of the mortar is due in part to the gradual absorption of carbon dioxid from the atmosphere, forming calcium carbonate, and, in part, probably to the action of the lime upon the sand (silica) forming a calcium silicate. The conversion of lime in mortar to the carbonate proceeds rapidly on the outside, but is incomplete, especially in the interior of the mortar. It is said that not all the lime of the mortar of the pyramids is yet converted into calcium carbonate.

Calcium Dioxid, CaO₂

278. Preparation.—This is prepared by adding hydrogen dioxid to lime-water. It loses half of its oxygen on heating. Calcium forms but one class of salts, and in these it is bivalent. These salts are more numerous and useful than those of magnesium. Among them are to be noted especially the carbonate (limestone), sulphate (gypsum), nitrate, phosphate (bones), and silicate.

Strontium Oxid or Strontia, SrO

279. Preparation and Properties.—Strontium forms two oxids. Strontia, SrO, is generally prepared by heating the nitrate. It is a grayish white powder uniting with water to form the hydroxid, $Sr(OH)_2$, which on being strongly heated turns back into the oxid. This hydroxid is soluble in hot water and has caustic and basic properties. It is used in sugar refineries.

Strontium Dioxid, SrO_2

This is prepared like calcium dioxid and has similar properties. The chief salts of strontium are the nitrate, chlorid, and carbonate.

Barium Oxid or Baryta, BaO

280. Preparation and Properties.—Barium forms two oxids, baryta, BaO, and barium dioxid, BaO_2. Baryta is best prepared by heating the nitrate. It is a grayish white mass, melting at a white heat and slaking in water with the evolution of heat. This gives the hydroxid, $Ba(OH)_2$. This is very stable, melting without decomposition. It crystallizes easily and is more soluble in water than calcium hydroxid, giving what is called baryta water, which is more alkaline than lime-water and is frequently used for absorbing carbon dioxid. This hydroxid is used in sugar refining. It is a poisonous body. The salts of barium are formed after the type of this oxid. The chief ones are the chlorid, nitrate, and sulphate.

Barium Dioxid, BaO_2

281. Preparation and Properties.—This is prepared by heating baryta to redness in a stream of dry oxygen or by heating the hydroxid in the air. The product is grayish, more porous and fusible than BaO, and combines with water to form a hydrate, $BaO_2.8H_2O$. On heating to bright redness half the oxygen is lost. As this oxygen will be taken up again at a lower temperature, this has been suggested as a means of preparing oxygen, but practical difficulties have prevented the successful carrying out of the method. The hydroxid is used for the production of hydrogen dioxid.

Experiment 111.—Heat calcium carbonate ($CaCO_3$) intensely on charcoal. Test the residue on moistened litmus paper. Heat and test barium carbonate ($BaCO_3$).

Experiment 112.—Breathe through a tube placed in a solution of calcium hydroxid. Repeat with barium hydroxid. What is formed in each instance? Which most readily and voluminously? Why?

THE SULPHIDS OF GROUP II

The sulphids of this group are formed by the action of carbon at a high temperature on the corresponding sulphates; thus,

$$CaSO_4 + 4C = 4CO + CaS.$$
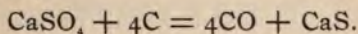
These sulphids possess the property of glowing in the dark after having been exposed to sunshine. They are the chief constituents of " luminous paint." Calcium sulphid for this purpose is formed by heating lime with sulphur.

Calcium sulphid is but sparingly soluble in water, while barium sulphid is much more soluble. When treated with hydrogen sulphid, the sulphids are changed into the hydrosulphids, which are soluble in water;

$$BaS + H_2S = Ba(SH)_2,$$

analogous to

$$BaO + H_2O = Ba(OH)_2,$$
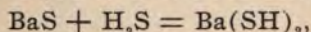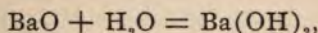
Calcium sulphid occurs as a waste product in the Le Blanc soda manufacture, and is utilized for the recovery of the sulphur.

OXIDS OF THE NEGATIVE SERIES OF GROUP II

These oxids differ from those of the first series in their not slaking in water and being less basic. The hydroxids are much less stable and are obtained by precip-

itation.   Only one of these elements has more than one
oxid.   Mercury has two.

Zinc Oxid, ZnO

282.   Preparation and Properties.—Zinc oxid occurs
as one of the ores of zinc under the name of zincite or
red zinc ore.   It can be prepared by burning the metal.
For medicinal use the carbonate is heated.   It is a heavy
white powder, yellow when hot and is insoluble in
water.   It is called zinc white and is used as a
paint.   The hydroxid, $Zn(OH)_2$, is obtained as a white
powder by adding an alkaline hydroxid to a solution of
a zinc salt and drying the precipitate.   It is insoluble
in water, loses water on heating, and is soluble in both
alkalies and acids.   Toward strong bases, $Zn(OH)_2$
acts as a weak acid forming salts soluble in water,
called zincates.

$$Zn(OH)_2 + 2NaOH = 2H_2O + Na_2ZnO_2.$$
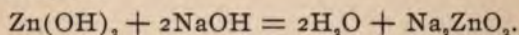
The most important zinc salts are the sulphate and
chlorid.   Zinc is bivalent in these compounds.

Experiment 113.—Treat a solution of zinc sulphate ($ZnSO_4$)
with a solution of sodium hydroxid.   Add an excess.

Cadmium Oxid, CdO

283.   Properties.—Cadmium oxid is obtained by burn-
ing the metal.   It is a brown powder, insoluble and very
infusible.   Cadmium hydroxid, $Cd(OH)_2$, is formed
as a white precipitate by adding an alkaline hydroxid
to a cadmium salt in solution.   It absorbs carbon dioxid
and is decomposed at 300°.   With acids the oxid or
hydroxid gives salts of cadmium in which cadmium is
bivalent.   The sulphate is the chief compound.

Experiment 114.—Heat a small piece of cadmium before the
blowpipe.   What is formed? Is it fusible or volatile?

Experiment 115.—Precipitate a solution of cadmium chlorid (CdCl$_2$) with sodium hydroxid. Filter and heat the precipitate in a porcelain crucible to a low red heat. Give the equation for the reaction.

Mercurous Oxid, Hg$_2$O

284. Properties.—This is the black oxid of mercury and is obtained by the action of alkalies upon mercurous compounds. It is a black powder which is changed by light or moderate heating into mercury and the higher oxid. It is insoluble in water. It gives mercurous compounds.

Mercuric Oxid, HgO

285. Preparation and Properties.—This is the red oxid and was known in early times as the red precipitate, or precipitate *per se*. It was prepared by heating mercury for a long time near its boiling-point or by heating it along with the nitrate. It is a very heavy, red solid, insoluble, poisonous, with an alkaline reaction, and decomposed by heating. If prepared by precipitation with an alkali it is an orange-yellow powder and in this form it is much more reactive with acids. This oxid forms the mercuric salts which are more stable than the mercurous.

Neither of these oxids seem to form hydroxids at ordinary temperatures. Below —42° HgOH is known. Here we have another element which forms two classes of salts as copper does. The interchange between them may be effected by similar methods to those given in the case of copper. The valence of mercury in these two classes would seem to correspond to that of copper. The mercurous salts are somewhat readily decomposed by light ; the mercuric are acted upon with less energy. The mercuric salts are the most

important. The chief compounds are the two chlorids, the sulphate, nitrate, and sulphid.

Experiment 116.—Treat a solution of mercurous nitrate ($HgNO_3$) with sodium hydroxid; mercuric nitrate ($Hg(NO_3)_2$) with sodium hydroxid. What is formed in each instance?

SULPHIDS OF THE NEGATIVE SERIES OF GROUP II

Zinc sulphid, zinc blende, ZnS, is the chief ore of zinc. Cadmium sulphid, greenockite, CdS, is a rare mineral, cadmium generally occurring in small quantities in the zinc blende of certain localities.

Mercuric sulphid, HgS, occurs in nature as cinnabar, and is the chief ore of mercury. It is formed artificially by (1) the sublimation of a mixture of mercury and sulphur;

$$Hg + S = HgS;$$
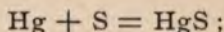
or (2) precipitation of mercuric solutions by hydrogen sulphid or other soluble sulphids;

$$HgCl_2 + H_2S = HgS + 2HCl.$$
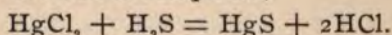
The precipitate is black, but from it the red form, the pigment vermillion, may be obtained. When obtained by sublimation, the pulverized sublimate is vermillion.

THE OXIDS OF GROUP III

These oxids are of the type M_2O_3. They or their hydroxids are widely distributed in nature. They are very stable and less basic than the preceding group. The hydroxids are formed by precipitation.

Boron Trioxid, B_2O_3

286. Preparation and Properties.—Boron forms but one oxid, boron trioxid, B_2O_3. It can be obtained by

burning boron in the air or by heating the hydroxid, $B(OH)_3$, which occurs naturally. It is a white hygroscopic solid which melts without decomposition and volatilizes at a white heat. It unites with water to form boric acid. Many metallic oxids dissolve at a red heat in boron trioxid giving glasses of characteristic colors.

287. Boron Hydroxid, Boric Acid, $B(OH)_3$.—This is formed by uniting the oxid with water or by decomposing borax with a mineral acid. It is found dissolved in the waters of certain lakes in Tuscany and is obtained largely from that source. It is a crystalline solid having a weak acid character, thus showing the analogy of boron, the bridge element, to the members of Group IV. It is volatile with steam and with alcohol. It colors the flame green. The salts are very unstable and few are known.

288. Metaboric Acid, $BO(OH)$.—This acid is produced by heating boric acid to 100°, thus being formed by the loss of water. It is a white powder, uniting with the positive elements of the first two groups to form salts called metaborates.

289. Formation of Boric Acids.—The steps in the formation of these acids from the oxid are as follows:

$$B_2O_3 + H_2O = 2HBO_2,$$
$$HBO_2 + H_2O = H_3BO_3;$$

or graphically,
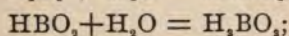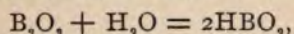
$$B\!\!\begin{array}{c} \diagup OH \\ \diagdown O \end{array} + HOH = B\!\!-\!\!OH\begin{array}{c} \diagup OH \\ \diagdown OH \end{array}.$$
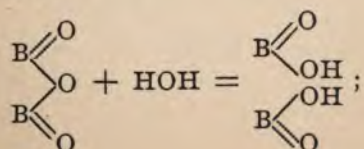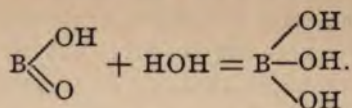
Orthoboric acid has the formula $B(OH)_3$, an *ortho*-acid being, in general, an acid in which the negative element (here boron) is united solely to hydroxyl groups. Metaboric acid is written $HO\!-\!B\!=\!O$, a *meta*-acid being formed from an *ortho*-acid by the loss of a molecule of water.

$$B\begin{array}{c} \diagup OH \\ -OH \\ \diagdown OH \end{array} - H_2O = B\begin{array}{c} \diagup\!\!\diagup O \\ \diagdown OH \end{array}.$$
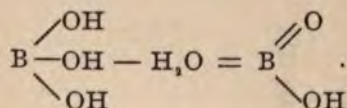
When orthoboric acid is heated to 100° it loses water, and the metaboric acid is formed. When metaboric acid is highly heated it loses water and boron oxid is formed.

290. Tetraboric Acid, $B_4O_5(OH)_2$.—This acid is made by heating boric acid a long time at a temperature of 140°. It gives tetraborates with the positive elements. These are the most stable and the best known of the compounds of boron. The most useful of these is sodium tetraborate, or borax, $Na_2B_4O_7$.

291. Borax.—This salt, crystallized with ten molecules of water, $Na_2B_4O_7.10H_2O$, is found in nature in certain springs and lakes, as the borax lakes of Nevada, and especially of Central Asia, from which a considerable supply comes into the market as *tincal*. It is a white crystalline solid, easily soluble in water. When heated, it swells up—intumesces—and loses its water of crystallization, forming a glassy mass, called borax glass. This

possesses the property of dissolving, when fused, many metallic oxids, some of which impart color to it, and hence the borax bead is often used in the laboratory for the detection of certain metals. When these oxids dissolve in borax, complex borates are formed. Borax may be considered as a salt of a hypothetical acid, $H_2B_4O_7$, derived from orthoboric acid by the loss of water.

$$4B(OH)_3 = 5H_2O + H_2B_4O_7.$$
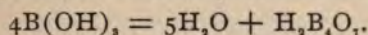
Borax and boric acid are quite strong antiseptics and are often used as food preservatives.

Experiment 117.—Make a concentrated solution of borax by dissolving it in a small amount of hot water. Cool the solution somewhat and cautiously add concentrated sulphuric acid. Boric acid will crystallize out in pearly scales. Pour the mixture into a porcelain dish, add an equal quantity of alcohol, warm, and then set fire to the alcohol. Notice the color of the flame.

Experiment 118.—Make a borax bead by fusing borax, with a blowpipe, on a loop of platinum wire (see Fig. 32). Place a bit of copper sulphate on the bead and re-fuse. Note the color of the bead.

Fig. 32.

292. Aluminum Oxid.—Aluminum forms but one oxid, alumina, Al_2O_3. This however forms several hydroxids. It is the typical oxid of the group.

Alumina, Al_2O_3
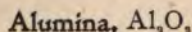
293. Occurrence and Properties.—This oxid occurs nearly pure in a number of minerals and in certain precious stones, as the ruby, sapphire, corundum, etc. It can be prepared by heating the hydroxid or by precipitation from alkaline aluminates by means of carbon dioxid.

$$2NaAlO_2 + CO_2 = Al_2O_3 + Na_2CO_3.$$
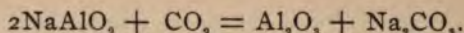
Alumina is a white powder which may be crystallized. It is insoluble in water but is soluble in strong acids if it has not been too strongly ignited. When crystallized it is very hard and is used for polishing glass, metal, etc. It is very stable and is not decomposed at a high temperature. It is dissolved by fused cryolite and in this solution may be decomposed by the electric current. This is the chief mode of preparing the metal.

294. Aluminum Hydroxids.—Several of these occur naturally as hydrargillite, $Al(OH)_3$, diaspore, $AlO(OH)$, and bauxite, $(AlFe)_2O(OH)_4$. It is obtained also as a gelatinous precipitate, $Al(OH)_3$, on adding an alkaline hydroxid to solutions of aluminum salts. Freshly precipitated, the hydroxid is easily soluble in acids, forming salts. It is used for the purification of water because of its power of removing suspended matter and even matter in solution. It is also used for fixing colors and for tanning. For these purposes some salt of aluminum is generally used, the hydroxid being precipitated from it.

295. Aluminates.—Towards strong bases aluminum hydroxid acts as an acid; thus, when dissolved in sodium hydroxid, sodium aluminate is formed.

$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O.$$
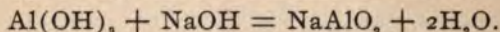
Sodium aluminate is a derivative of a hypothetical meta-aluminic acid, $HO—Al=O$. Several salts of this acid are found in nature, as spinel, $Mg(AlO_2)_2$, chrysoberyll, $Gl(AlO_2)_2$, gahnite, $Zn(AlO_2)_2$. Sodium aluminate is produced in preparing alumina from bauxite. It is used as a mordant.

296. Salts of Aluminum.—There is but one class of

aluminum salts. In these the element is trivalent. Many of these salts are very useful, as the sulphate and double sulphates or alums, the chlorid, nitrate, and acetate.

Experiment 119.—Precipitate a solution of alum $(KAl(SO_4)_2)$ with sodium hydroxid and note the effect of an excess of the reagent.

OXIDS OF THE REMAINING ELEMENTS OF GROUP III

297. Properties.—In the Positive Series of this group we have a number of rare elements. These all form basic sesquioxids like that of aluminum. They are too rare for separate mention. In the Negative Series the first two, gallium and indium, are also rare and need not be described as they follow closely the type, aluminum. The third member, thallium, is not so rare, though still seldom met with. Like most elements of very high atomic weight, it departs from the type in some respects. It shows analogies to its two neighbors, gold and lead. Thus it forms two oxids, Tl_2O and Tl_2O_3. The first corresponds to aurous oxid, cuprous oxid, etc., of the first group so that at first chemists, for this and other reasons, were inclined to classify this element with the alkalies. It gives a well-defined series of salts called *thallous*. Of these the sulphate and the chlorid are the most important. Thallium also forms a trioxid, Tl_2O_3, analogous to aluminum trioxid, and there is a series of *thallic* salts derived from it.

THE SULPHIDS OF GROUP III

Very few sulphids of these elements are known and none can be formed by precipitation with hydrogen sulphid or ammonium sulphid.

Aluminum Sulphid, Al_2S_3

298. Properties.—Aluminum sulphid can be formed only in the dry way as it is decomposed by water or even the moisture of the air. When a soluble sulphid is added to an aluminum salt the hydroxid is precipitated.

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O =$$
$$2Al(OH)_3 + 3(NH_4)_2SO_4 + 3H_2S.$$
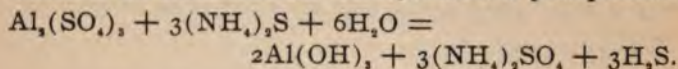
THE OXIDS OF GROUP IV

299. General Characteristics.—This is the first of the distinctively acid-forming groups, though some acid-forming oxids, as B_2O_3, have already been met with. As the atomic weight increases, this acid character becomes less pronounced. The typical oxid is MO_2. The elements of the Positive Series show greater analogy to the type than the elements of the Negative Series. Most of these oxids are white solids and many of them occur in nature. The typical oxids can be prepared by burning the elements, or by heating the hydroxids or any salts of volatile acids.

300. Carbon Oxids.—There are two oxids formed by carbon, carbon monoxid, CO, and carbon dioxid, CO_2. The latter is the typical oxid.

Carbon Monoxid, CO

301. Preparation.—Carbon monoxid is formed by burning carbon in insufficient oxygen or by passing carbon dioxid over hot carbon.

$$CO_2 + C = 2CO.$$
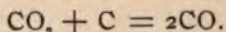
It can be more conveniently prepared, for class purposes, by heating oxalic acid with sulphuric acid.

$$H_2C_2O_4 = CO + CO_2 + H_2O.$$
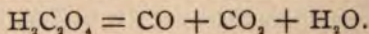
It is formed for industrial purposes by the action of steam on heated coke. Hydrogen is liberated at the same time.

$$H_2O + C = CO + H_2.$$
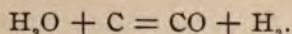
This mixture is known as water-gas or fuel-gas and has an extensive use for heating purposes. It burns with a very hot, pale blue flame and hence cannot be used for illuminating purposes unless enriched with hydrocarbons or used in a Welsbach burner. This burner is provided with a mantle containing such oxids as those of thorium and zirconium. These become incandescent when heated by the burning gas and give a brilliant light.

302. Properties.—It is a colorless, tasteless gas with a very slight odor, a little lighter than air, hard to condense, and nearly insoluble in water. It burns with a blue flame to carbon dioxid and combines with certain metals as nickel, but does not form an acid with water. It is poisonous when breathed.

Carbon Dioxid, CO_2

303. Preparation.—This body is prepared by the burning of carbon or any substance containing carbon. It is also set free on heating limestone (calcium carbonate). On a smaller scale it is obtained by the action of acids upon metallic carbonates.

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$
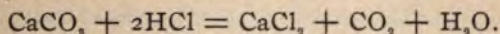
This may be carried out in a Kipp generator (see Fig. 33). Calcium carbonate is placed in the middle division and dilute hydrochloric acid poured in at the top. This acid rises into the middle division and the action begins. When the exit of the gas is cut off, the pressure forces the acid back again.

304. Occurrence.—Carbon dioxid occurs in the atmosphere, averaging about three parts in 10,000 parts of air. It comes into the air from the breathing of animals, decay of organic matter, and from fires. It is removed from the atmosphere by plants, which assimilate it, using it in the construction of new tissue, and also by solution in water and the formation of carbonates. It is supposed, at present, that these different agencies for supplying and removing carbon dioxid from the air about balance one another. Carbon dioxid is also found in volcanic regions, coming most probably from the decomposition of carbonates. In the same way it is formed in lime kilns where limestone is being "burned." It is also met with in vats where fermentation is going on, as in wine-cellars and breweries.

Fig. 33.

305. Properties.—Carbon dioxid is a colorless gas with a slight acid taste. It has a specific gravity of 1.5 and is somewhat soluble (volume for volume) in water, so that, in its preparation, it is not caught over a pneumatic trough but by displacement. The supersaturated solution in water, made under pressure, is used for effervescing drinks.

Carbon dioxid can be condensed to a liquid with comparative ease and frozen to a solid by its own evaporation. It does not support combustion but extinguishes flame.

It is not actively poisonous but causes death by excluding oxygen. By passing it over hot carbon it is reduced to carbon monoxid. Some very powerful combustions can continue in carbon dioxid, showing that at a high temperature the carbon and oxygen are dissociated. It can also be decomposed by the passage of electric sparks through it. Still it is a very stable compound. This is an acid-forming oxid. The solution in water is weakly acid, reddening blue litmus and combining with various oxids to form carbonates. These carbonates are, many of them, very widely distributed in nature and form a very useful class of salts. Most of them are insoluble in water and are easily decomposed by heating or by the addition of another acid. Carbonic acid is one of the weakest of the acids. The free acid, H_2CO_3, does not seem to exist, at least apart from its solution in water.

Experiment 120.—Treat calcium carbonate with hydrochloric acid. Lead the evolved gas into lime-water. Test the gas as to combustibility.

306. Oxyacids.—While boric acid was the first of the oxyacids which we have met, it is perhaps better to discuss the general characteristics of this class of acids and their derivatives after the study of carbonic acid, as it furnishes a fuller illustration. Oxyacids are formed by the union of negative oxids with water, though sometimes this union cannot be brought about directly. They answer the chief test for acids, uniting with bases to form salts.

In these acids one or more hydroxyls (OH) are supposed to be united with the negative element. The hydrogen of the hydroxyl is replaceable by a positive element. When there is only one such replaceable hydrogen atom the acid is said to be monobasic (capable of

combining with one unit of base); when there are two it is dibasic, etc. Thus carbonic acid is dibasic, $OC(OH)_2$, phosphoric acid is tribasic, $OP(OH)_3$, etc.

Carbonic acid, or any dibasic acid, can form two classes of salts. First, when both of the hydroxyls have their hydrogen replaced by a positive element and the acid is fully neutralized, the salt is called a normal salt. Secondly, when only one is replaced the acid is only partly neutralized, an acid salt or, in the case of carbonic acid, a bicarbonate is the resulting product. Of course, it is also possible to regard these salts from a different point of view, looking upon them as being formed by the replacement of the hydrogen in a basic hydroxid by means of an acid radical. Thus we can have mon-acid, di-acid, tri-acid, etc., bases, and if only one hydrogen of a di-acid, tri-acid, etc., base is replaced, a basic salt results. A full neutralization yields a normal salt.

CARBONATES OF GROUP I

We will consider next the compounds of carbonic acid, called carbonates, taking them up in the order of the several groups. The carbonates of Group I are as a rule white, crystalline solids, soluble in water, having an alkaline reaction and stable up to the temperature of melting. The carbonates of the Negative Series, however, do not follow this description of the type. These carbonates may, in general, be formed by the action of carbon dioxid upon the oxids or hydroxids. The generic formula is M_2CO_3 for the normal carbonates and $MHCO_3$ for the acid or bicarbonates. The most important carbonate of the group is that of the type.

307. Sodium Carbonate, Na_2CO_3.—This occurs in nature as *natrona* dissolved in the water of certain lakes

in Egypt, South America, and the United States. This was the chief source in early times. It was also obtained from the ash of sea-weeds which were collected and burned along the coasts of Great Britain, France, and Spain. These sources could not supply the very large demand for this important substance in modern times and so it is now manufactured on a large scale. Its manufacture is known as the alkali industry. There are two chief processes for its manufacture, both starting with common salt, NaCl, the most abundant and cheapest compound of sodium.

308. Preparation of Sodium Carbonate. The Le Blanc Process.—This was the first process in use but it is now, in a measure, supplanted by the ammonia-soda process. The salt is first changed into sodium sulphate, then into sodium sulphid, and lastly into sodium carbonate, according to the following reactions:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$
$$Na_2SO_4 + 4C = Na_2S + 4CO.$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$
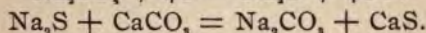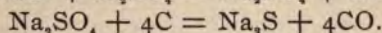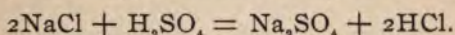
Sodium chlorid is first heated with sulphuric acid. This gives sodium sulphate and hydrochloric acid. This sodium sulphate is then mixed with carbon and chalk and heated in a furnace. The sodium carbonate can then be dissolved out with water and purified by crystallization. This gives crystallized soda or sal soda, $Na_2CO_3.10H_2O$.

309. The Solvay, or Ammonia-Soda Process.—In this process ammonia, carbon dioxid, and water are brought together to form ammonium bicarbonate.

$$NH_3 + H_2O + CO_2 = NH_4HCO_3.$$
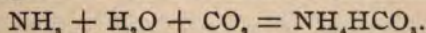
When this comes in contact with a solution of sodium

chlorid, sodium bicarbonate is formed, owing to its lesser solubility, and ammonium chlorid.

$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$
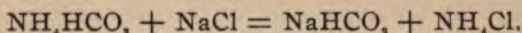
The ammonia is recovered from the ammonium chlorid by heating with lime and is used over again.

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$
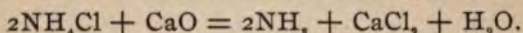
As seen above, this process yields the bicarbonate instead of the carbonate. This bicarbonate, as it retains traces of ammonia, is changed into the carbonate by gentle heating.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$
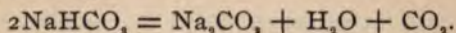
The reverse change is also easily carried out.

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$
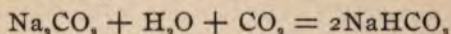
310. Properties.—Sodium carbonate crystallizes with water, and melts at a red heat losing some of the carbon dioxid and forming sodium hydroxid. It has a strongly alkaline reaction and taste. It is known as soda-ash, sal soda, and washing-soda, and is used in many manufactures, as in the making of glass, paper, soap, etc.

311. Sodium Bicarbonate, or Hydrogen Sodium Carbonate, $NaHCO_3$, is less alkaline, less soluble in water, and is decomposed into the normal carbonate on gentle heating. It is called cooking-soda and has many uses on account of the large amount of carbon dioxid contained in it and its feebler alkaline or basic nature. It is one of the chief constituents of baking-powders. The addition of a strong acid to either of these carbonates causes an abundant evolution of carbon dioxid.

312. Potassium Carbonate, K_2CO_3.—This was, for a long time, obtained chiefly from the ashes of land plants by lixiviation. It was hence called potash. When

purified by calcination and recrystallization it was known as pearlash. The impure form, containing a good deal of water, is called potash-lye. Potassium carbonate is now made from potassium chlorid by a modified Solvay process in which trimethylamine is substituted for ammonia.

313. Other Alkaline Carbonates.—Lithium carbonate, Li_2CO_3, is the only one of these carbonates which is not readily soluble. It is only slightly soluble in water and resembles the carbonates of Group II. Rubidium and cesium carbonates resemble those of potassium.

CARBONATES OF THE NEGATIVE SERIES OF GROUP I

These differ very decidedly from the alkaline carbonates in solubility, stability, mode of preparation, etc. The copper carbonates are found in nature as malachite, $CuCO_3.Cu(OH)_2$, and azurite, $2CuCO_3.Cu(OH)_2$. Copper carbonates may be formed by the action of carbon dioxid and water upon copper or by precipitation with an alkaline carbonate from a solution of a copper salt. Only basic carbonates are known, and these are insoluble in water and decomposed by heating. The normal carbonate of silver is formed by precipitation.

$$2AgNO_3 + Na_2CO_3 = Ag_2CO_3 + 2NaNO_3.$$
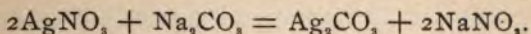
It is insoluble and is easily decomposed by heat or acids.

CARBONATES OF GROUP II

The carbonates of Group II generally occur naturally. They can be prepared by precipitation with an alkaline carbonate and are white powders, nearly insoluble in water and decomposed by acids and heating. They are also formed by the action of carbon dioxid upon the oxids or hydroxids.

314. Magnesium Carbonate, $MgCO_3$.—This is found as magnesite, or combined with calcium carbonate as dolomite. By precipitating a solution of magnesium sulphate with sodium carbonate, a basic carbonate is formed called *magnesia alba* which is used medicinally. Its exact nature depends upon the conditions of precipitation, as temperature, concentration of solution, etc. Magnesium carbonate is a white powder, insoluble in water though soluble in water containing an excess of carbon dioxid. It changes to the oxid on being heated.

315. Calcium Carbonate, $CaCO_3$.—This occurs in many forms and under many names in nature. Calcite, Iceland spar, arragonite, limestone, marble, coral, shell, chalk, marl, are all names for calcium carbonate in a greater or less state of purity. It is prepared by precipitation and is known as precipitated chalk and used medicinally and for polishing. It may further be formed by passing carbon dioxid through lime-water. The oxid or hydroxid will also absorb carbon dioxid from the air and so become " air-slaked." The pure carbonate is a white powder decomposed by heat and acids, nearly insoluble in water, but soluble in water containing an excess of carbon dioxid. This gives " hard water." The excess of carbon dioxid may be driven off by agitation of the water or by boiling it. Hence the water is said to be temporarily hard. Upon this action depends the cave formation found in all limestone regions. Water, especially after having leached down through the soil, contains carbon dioxid in solution, and making its way through the limestone gradually dissolves it, taking it into solution in the form of hydrogen calcium carbonate, or calcium bicarbonate, $Ca(HCO_3)_2$. In this way caves are first excavated.

This water, dripping from the roofs of caves, loses the carbon dioxid and this causes the precipitation and deposition of the calcium carbonate which was held in solution. Such deposits depending from the roof of a cavern are known as stalactites, while those built up from the floor are stalagmites. The carbonate is used for fertilizing purposes and the crystals of calc-spar are used for optical purposes.

316. Other Carbonates of Group II.—Strontium carbonate, $SrCO_3$, found as strontianite, and barium carbonate, $BaCO_3$, found as witherite, have properties similar to those of calcium carbonate. Barium carbonate is more insoluble and both are more difficult to decompose by heating. In the Negative Series, zinc carbonate is found as calamine and is an important ore of zinc. Basic zinc carbonates are known.

Experiment 121.—Add sodium carbonate to solutions of magnesium sulphate, calcium chlorid, and barium chlorid. What is formed in each case?

CARBONATES OF GROUP III

The elements of this group do not show much tendency to form carbonates. On attempting to precipitate an aluminum carbonate by means of an alkaline carbonate the hydroxid will be formed instead.

We have seen that carbonic acid, H_2CO_3, is too unstable to exist alone (unless it be in solution in water), readily giving off carbon dioxid. Many carbonates share this property and are readily decomposed by water with the loss of more or less of their carbon dioxid, giving rise to basic carbonates or even hydroxids or oxids. The strongly positive elements alone, such as we have considered, are able to hold an equivalent amount of carbon dioxid. For example, when sodium carbonate acts upon a solution of lead acetate, the normal

carbonate is not formed, but a basic carbonate, partly at least in composition $2PbCO_3.Pb(OH)_2$. We may consider the reaction as involving two distinct reactions; *viz.*,

$$3Pb(C_2H_3O_2)_2 + 3Na_2CO_3 = 3PbCO_3 + 6Na(C_2H_3O_2).$$

$$
\begin{matrix}
PbCO_3 \\
PbCO_3 \\
PbCO_3
\end{matrix}
+ 2HOH =
\begin{matrix}
& Pb \begin{matrix} OH \\ CO_3 \end{matrix} \\
& Pb \begin{matrix} CO_3 \\ OH \end{matrix}
\end{matrix}
+ H_2CO_3 \text{ (or } H_2O + CO_2).
$$
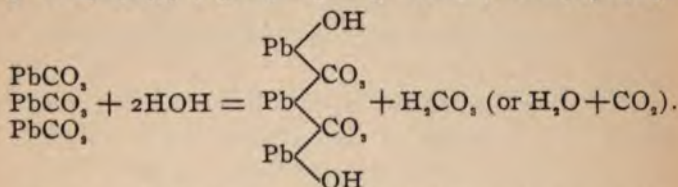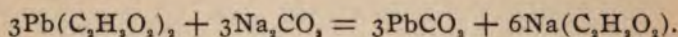
When a salt of aluminum is similarly acted upon, a hydroxid is formed.

$$2AlCl_3 + 3Na_2CO_3 + 6H_2O =$$
$$2Al(OH)_3 + 6NaCl + 3H_2O + 3CO_2.$$
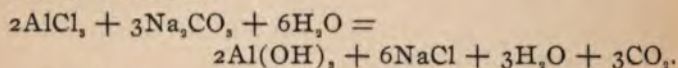
Experiment 122.—Add sodium carbonate or ammonium carbonate to solutions of lead acetate $(Pb(C_2H_3O_2)_2)$ and aluminum sulphate $(Al_2(SO_4)_3)$. What is evolved?

CARBONATES OF GROUP IV

No definite carbonates are known in this group except in the Negative Series. Here lead carbonate is the most important. It is found as one of the ores of lead and is called cerussite. But the artificially prepared basic carbonate, called white lead, $2PbCO_3.Pb(OH)_2$, is one of the most useful of the carbonates. There are a number of different processes by which it is prepared; only one will be given.

317. Preparation of White Lead—Dutch Process. —Rolls or buckles of thin lead are piled in an earthen pot, the bottom of which contains vinegar or dilute acetic acid. A layer of these is placed in a large bin, covered with boards and then with several inches of

manure, or spent tan bark. On this is placed another layer of pots, etc., until the bin is filled. This is left several weeks. Heat, generated by the fermentation of the manure, partially volatilizes the acetic acid, which acts upon the lead, converting it into a basic lead acetate. This is, in turn, acted upon by the carbon dioxid generated by the fermenting manure, forming the basic carbonate of lead or white lead. The reaction proceeds from the surface of the lead inwards till it is more or less completely converted into the basic carbonate. This is then cleansed and ground in oil. This is the chief process in use. White lead is the chief white paint, having greater covering power than such substances as zinc white. It is discolored by hydrogen sulphid.

CARBONATES OF THE REMAINING GROUPS

With regard to the remainder of the groups, carbon dioxid does not combine except with certain of the elements of their first or Positive Series or with some of those having large atomic weights. Thus there is a manganese carbonate, $MnCO_3$, and several basic bismuth carbonates as $(BiO)_2CO_3$. There are also carbonates of the iron series. Thus siderite, $FeCO_3$, is one of the ores of iron. The basic carbonate of iron is also often seen. The bicarbonate of iron is held in solution in water containing an excess of carbon dioxid. Such waters are called chalybeate. On losing the excess of carbon dioxid the iron is deposited as a red slime, or mud, consisting of the basic carbonate and hydroxid. All of these carbonates are insoluble in water and are decomposed by heating and by acids.

318. Sulphids of Carbon.—Several of these compounds probably exist, but the only important one is

carbon disulphid, CS_2. This corresponds to carbon dioxid and is formed by the direct union of the elements, sulphur vapor being led over heated coke.

$$C + 2S = CS_2.$$
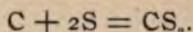
When pure, carbon disulphid is a colorless, rather pleasant smelling liquid, but it is usually somewhat colored and has a very disagreeable odor. It refracts light strongly, boils at 47°, and remains a liquid down to —110°. It is insoluble in water but is itself a solvent for fats, oils, sulphur, phosphorus, iodin, etc. It burns with a blue flame to carbon dioxid.

Experiment 123.—Examine carbon disulphid and test as to its solvent power with iodin and sulphur.

319. Thiocarbonic Acid.—Corresponding to carbonic acid, H_2CO_3, there is an acid, H_2CS_3, thiocarbonic acid, which may be looked upon as formed by the union of carbon disulphid and hydrogen sulphid. This is analogous to the formation of carbonic acid by the union of carbon dioxid and water. This acid is very unstable, but like carbonic acid forms a series of stable salts, the thiocarbonates, the best known of which is calcium thiocarbonate, $CaCS_3$. Salts of the ortho-thiocarbonic acid, $C(SH)_4$, are also known.

Silica, SiO_2

320. Occurrence.—Silicon forms but one oxid and this oxid is known as silica; it is an extremely important constituent of the earth's surface whether free or combined.

1. It occurs free in many forms: Rock-crystal, quartz, flint, sand, agate, etc. It forms a number of the precious stones as chalcedony, bloodstone, moss-agate, etc. It may be prepared in an amorphous condition by heating the hydroxid which is obtained by precipitation.

2. Combined silica is seen in the silicates. These are very numerous and complex in composition. Probably the most abundant is clay, then feldspar, mica, and many others.

321. Properties.—Silica is insoluble in water and acids except hydrofluoric acid ; it is soluble in alkalies. It has a specific gravity of 2.5 and melts only at the highest temperatures. Amorphous silica is a white powder ; crystallized silica is transparent like glass. It is very hard and brittle.

322. Silicon Hydroxids or Silicic Acids.—Silicon hydroxid, $Si(OH)_4$, is obtained by precipitation from solutions of alkaline silicates by means of an acid. When such a silicate is acted upon by an acid, an almost colorless, gelatinous mass is obtained, which in some cases has, even when filtered off and dried to a white powder, the formula $Si(OH)_4$, orthosilicic acid. It easily loses water forming $SiO(OH)_2$, metasilicic acid, and silica, SiO_2, is formed on complete dehydration.

$$K_4SiO_4 + 4HCl = 4KCl + H_4SiO_4.$$

$$Si\begin{cases}OH\\OH\\OH\\OH\end{cases} = Si\begin{cases}OH\\\\O\\OH\end{cases} + H_2O$$

$$\text{and } Si\begin{cases}OH\\\\O\\OH\end{cases} = Si\begin{cases}O\\\\O\end{cases} + H_2O.$$
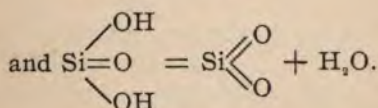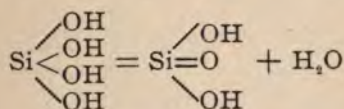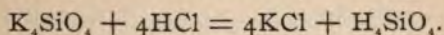
All of the silicic acid does not separate out as a gelatinous precipitate, some remaining in solution in the water. The silicic acids are insoluble in acids, but easily soluble in alkalies, forming silicates with them.

Experiment 124.—Add hydrochloric acid to a solution of potassium or sodium silicate (Na_4SiO_4). What is formed? Then add an excess of sodium hydroxid.

323. Silicates.—The great mass of the earth's surface is made up of silicates, limestones being the chief additional formation. While silicic acid is unstable and a weak acid, the silicates are very stable. The silicates of the alkalies are the only ones soluble in water; many silicates are soluble in hydrochloric acid with the separation of silicic acid; all are acted upon by hydrofluoric acid, though some only slightly. Many can be decomposed only by fusion with alkalies or alkaline carbonates.

The silicates are rarely derived from orthosilicic acid, H_4SiO_4; more frequently they are derived from metasilicic acid, H_2SiO_3; but by far the greater number are derived from complicated, hypothetical silicic acids somewhat like the boric acids. These polysilicic acids are themselves not known but their salts are.

TYPES OF SILICIC ACIDS.
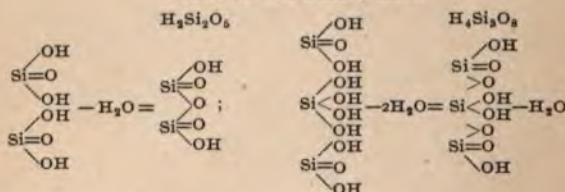
TYPES OF NATURAL SILICATES.
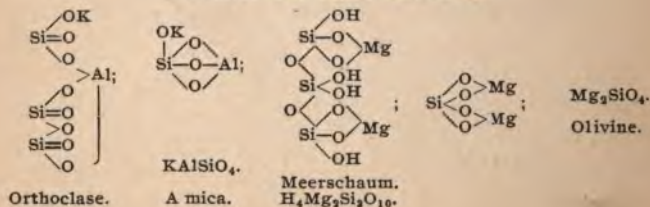
324. Glass.—The soluble silicates, potassium silicate, K_4SiO_4, and sodium silicate, Na_4SiO_4, are formed by fusing together potassium hydroxid or sodium hydroxid, or the carbonates, with quartz or sand. These are known as water-glass.

Ordinary glass is a mixture of the silicates of two or more of the following bases: soda, lime, potash, or lead. Common window glass is formed by melting together, sand, lime, and some sodium salt as the sulphate or

Fig. 34.

carbonate. This melting is done in a furnace in either a covered or an open glass pot (see Fig. 34). Impurities as iron and aluminum are often present and the glass may be further colored by various metallic oxids.

325. Porcelain and Earthenware.—We have seen that clay is a hydrogen aluminum silicate, being derived from feldspar, a potassium, sodium, or calcium aluminum silicate, by the washing out of the alkali. Various impurities are generally present in clay, such as iron oxid or hydroxid, calcium carbonate, etc. When clays are heated, water is driven off and a hard, porous, difficultly fusible or infusible mass is left. This is seen in bricks, earthenware, etc. If iron is present it gives the bricks a red color. In making porcelain only the purest clay can be used. This is called kaolin. It is mixed with ground feldspar.

Objects made of clay are generally covered with a glaze to make them impermeable to water. The glaze is a glass made of easily fusible silicates, often of feldspar or lead silicate.

326. Silicon Sulphids.—Two sulphids of silicon are known, SiS and SiS_2. These are mentioned to show the analogy to the oxygen compounds.

Titanium Oxids

327. Titanium Dioxid, TiO_2.—Titanium has one chief oxid, TiO_2. This resembles silica and can be prepared in the same way. It is a white insoluble powder. It is found free, as rutile, etc., and also occurs combined with various bases as titanates. These show an analogy to the silicates. It is very frequently found in iron ores and in small amount is very widely distributed in soils, etc. There are several hydroxids of titanium as of silicon. The normal hydroxid is $Ti(OH)_4$. These hydroxids possess acid properties. A monoxid of titanium, TiO, is also known.

Zirconium Oxids

328. Zirconium Dioxid, ZrO_2.—Much the most important is the typical oxid, ZrO_2, zirconia. Though occasionally found free, it generally occurs combined with silica in the zircon. When pure this is highly prized as a precious stone, the hyacinth or jacinth. Zirconium hydroxid, $Zr(OH)_4$, is a weak acid toward strong bases and a weak base toward acids. Zirconia is used to some extent in incandescent gas burners.

Thorium and Germanium Oxids

Thorium forms a dioxid, thoria, ThO_2. It resembles the other dioxids of the group, particularly that of tita-

nium. The hydroxid, however, has lost the characteristics of an acid and acts only as a base. The chief use for thoria is in the incandescent gas burners. Germanium forms a dioxid, GeO_2.

Tin Oxids

329. Stannous Oxid, SnO.—Tin forms two oxids, stannous oxid, SnO, and stannic oxid, SnO_2. Stannous oxid is prepared by heating stannous oxalate without access of air. It is an olive-colored powder, blackens on exposure to sunlight, takes fire when heated in the air, absorbs oxygen readily, and gives, with acids, stannous salts. These have a metallic taste, redden litmus, absorb oxygen, and change into stannic salts. Hence they are used as reducing agents. A hydroxid, $Sn_2O(OH)_2$, is known.

330. Stannic Oxid, SnO_2.—This occurs in nature as tinstone and is the chief ore of tin. It is also called cassiterite and is a very heavy mineral. It may be artificially prepared by burning the element in the air and also by the action of nitric acid upon the metal with subsequent ignition of the product. It is a white powder, insoluble in water and most acids and having a specific gravity of 6.7. It forms two hydroxids, $SnO(OH)_2$ and $Sn_5O_5(OH)_{10}$.

331. Stannic Hydroxids.—The first of these, stannic acid, H_2SnO_3, forms stannates with the alkalies. Sodium stannate is used as "preparing salts" in calico-printing. Metastannic acid, $H_{10}Sn_5O_{15}$, which is polymeric with stannic acid, is insoluble in all acids except hydrochloric acid. With the alkalies it gives metastannates. Certain of these find use in calico-printing.

Thus there are four classes of compounds of tin : The two classes just mentioned, in which this element is neg-

ative and its hydroxids play the part of acids, and two classes in which it is positive giving stannous and stannic salts. The most important compounds are stannous and stannic chlorids and sodium stannate.

Experiment 125.—Precipitate a solution of stannous chlorid, $SnCl_2$, with sodium hydroxid, then add an excess of the precipitant.

Experiment 126.—Treat a little tin with concentrated nitric acid. What is formed?

Tin Sulphids

332. Stannous and Stannic Sulphids.—These two sulphids correspond to the oxids. They have the formulas SnS and SnS_2 respectively. They are formed by the precipitation of stannous or stannic salts by hydrogen sulphid. Stannic sulphid dissolves in solutions of alkaline sulphids with the formation of thio-salts.

$$SnS_2 + Na_2S \ = \ S{=}Sn{\Big\langle}{\begin{array}{l} S{-}Na \\ S{-}Na \end{array}}.$$
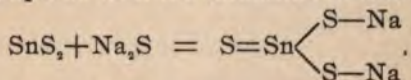
This is sodium thiostannate and corresponds to sodium stannate, $O{=}Sn{\Big\langle}{\begin{array}{l} O{-}Na \\ O{-}Na \end{array}}$. When treated with an acid

the thiostannic acid, $S{=}Sn{\Big\langle}{\begin{array}{l} SH \\ SH \end{array}}$, which should be

formed, at once decomposes into stannic sulphid, SnS_2, and hydrogen sulphid, H_2S, which is evolved.

Stannous sulphid is not soluble in sodium or ammonium sulphid, $(NH_4)_2S$, but is soluble in the disulphid, $(NH_4)_2S_2$, the extra sulphur atomc hanging the stannous salt to a stannic.

$$SnS + (NH_4)_2S_2 \ = \ S{=}Sn{\Big\langle}{\begin{array}{l} SNH_4 \\ SNH_4 \end{array}}.$$
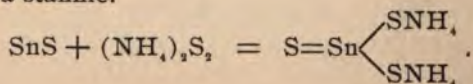
The thiostannates are soluble in water and their formation is made use of in separations in qualitative analysis.

Experiment 127.—Precipitate a few cubic centimeters of stannous chlorid solution with hydrogen sulphid (gas). After allowing to settle, pour off the supernatant liquid and add to the precipitate a small amount of ammonium sulphid (yellow, $(NH_4)_2S_x$). Warm gently until the soluble ammonium thiostannate is formed. Acidify with hydrochloric acid. Note the evolution of gas and precipitation of stannic sulphid.

Experiment 128.—Repeat the experiment using a solution of stannic chlorid in the place of stannous chlorid and using colorless ammonium sulphid, $(NH_4)_2S$, in place of the yellow. What differences are observable?

Lead Oxids

333. Lead Monoxid, Litharge, PbO.—This oxid is formed by heating lead in the air. It is known as litharge or massicot. It is a heavy yellow buff to reddish yellow powder, stable when heated alone, easily reduced by heating with carbon or hydrogen, insoluble in water; but a basic hydroxid can be prepared by the action of air and water upon the metal. This oxid is used in making red lead, glass, etc. It is a basic oxid and forms salts with the acids, giving the only well-characterized class of lead compounds. The chief salts are lead nitrate, acetate (sugar of lead), and the basic carbonate (white lead).

334. Red Lead, Minium, Pb_3O_4.—This is prepared by carefully heating the lead monoxid in the air. It is a brilliant red crystalline powder, with a specific gravity of 8.6 to 9.1. It forms no hydroxid and is decomposed by acids. It seems to be a compound of lead monoxid and lead dioxid,

$$2PbO + PbO_2 = Pb_3O_4,$$
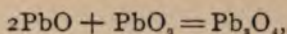
or a lead salt of orthoplumbic acid,

$$\begin{array}{c} Pb{<}^O_O{\Large>}Pb. \\ Pb{<}^O_O \end{array}$$
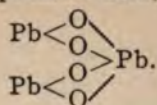
It is used as a paint and in glass-making, and is one of the most useful compounds of lead.

335. Lead Dioxid, PbO_2.—This oxid is prepared by treating red lead with nitric acid or chlorin. It occurs naturally in small quantities as plattnerite. It is a brown powder and decomposes on heating into the monoxid and oxygen. It shows a strong oxidizing power. A corresponding chlorid of lead has been formed, hence this oxid seems to act as a weak base. It also forms a hydroxid, $PbO(OH)_2$, called metaplumbic acid, which gives plumbates with a few strong bases, but these bodies are imperfectly known.

336. Other Lead Oxids.—Lead suboxid, Pb_2O, is a black powder, easily decomposed by heat. Lead sesquioxid, Pb_2O_3, may be considered a compound of the monoxid and the dioxid, or the lead salt of metaplumbic acid.

$$O=Pb+ \begin{array}{c} O \\ {\Large>}Pb \\ O \end{array} = O{=}Pb{\Large<}^O_O{\Large>}Pb$$
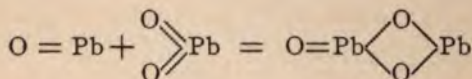
Lead metaplumbate.

It is a yellow powder. It forms no class of compounds and possesses no special importance.

337. Lead Sulphid.—Lead forms but one sulphid, PbS, galena, corresponding to the monoxid, PbO. This is an abundant mineral and is the chief ore of lead. It is a heavy black insoluble body.

Experiment 129.—Heat lead on charcoal with the blowpipe. What is formed?

Experiment 130.—Treat a little red lead or lead dioxid with concentrated hydrochloric acid. What is evolved? Why?

THE OXIDS OF GROUP V

338. General Characteristics.—These oxids are of two types, M_2O_3 and M_2O_5, though other oxids are formed. They are either neutral or acid-forming until a high atomic weight is reached. Base-forming oxids are also known for the elements of the first or Positive Series, and are often their chief oxids. These differ notably from the oxids of Group IV in seldom occurring uncombined in nature.

339. Nitrogen Oxids.—Nitrogen forms five oxids, the monoxid, N_2O, dioxid, NO or N_2O_2, trioxid, N_2O_3, tetroxid, NO_2 or N_2O_4, and pentoxid, N_2O_5. There are also three acids formed.

Nitrogen Monoxid, Nitrous Oxid, N_2O

340. Preparation and Properties.—This oxid is prepared by heating ammonium nitrate.

$$NH_4NO_3 = N_2O + 2H_2O.$$
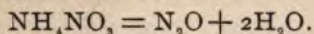
It is a colorless gas with a pleasant smell and sweet taste and a specific gravity of 1.5. It is somewhat soluble in water and alcohol and must therefore be caught over warm water in which it is very slightly soluble. It can be condensed by considerable cold and pressure, forming a liquid which boils at —80° and is used for the production of very low temperatures. Nitrogen monoxid supports combustion if it has been already actively started and is energetic enough to dissociate the nitrogen and oxygen. Thus a taper may be

extinguished while phosphorus burns very brilliantly. It can be breathed, producing insensibility. It is called "laughing gas" and is used as an anesthetic for minor operations. Though somewhat soluble in water it does not combine with it directly and so form a hydroxid.

Experiment 131.—Heat ammonium nitrate in a test-tube and by means of a delivery-tube collect the evolved gas. Test it as to odor, taste, and combustibility.

341. Hyponitrous Acid, HNO.—This acid would correspond to the hydroxid formed from the oxid just described. It must be prepared indirectly. A hyponitrite is first prepared by reducing a nitrite with sodium amalgam and this hyponitrite is then decomposed by means of an acid. It is a very weak and unstable acid and from its reactions cannot be considered a hydroxid of nitrous oxid.

Nitrogen Dioxid or Nitric Oxid, NO

✝**342. Preparation and Properties.**—This oxid is prepared by the action of certain metals, as copper, upon nitric acid.

$$3Cu + 8HNO_3 = 2NO + 3Cu(NO_3)_2 + 4H_2O.$$
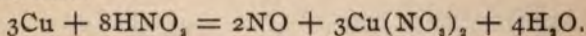
It is a colorless gas with a specific gravity of 1.089. It is condensed with difficulty and gives brown-red fumes on coming in contact with the air or oxygen, from the formation of higher oxids of nitrogen. It supports combustion but less readily than the preceding gas as it is dissociated at a higher temperature. Thus, burning sulphur will be extinguished in it but phosphorus will continue to burn. It is poisonous when breathed. With carbon disulphid it burns giving a very brilliant flame. It forms no hydroxid and no acid. It is insoluble in water but readily soluble in a solution of ferrous sulphate, which it colors brown.

Experiment 132.—To copper in a test-tube add a little water and an equal amount of concentrated nitric acid. Collect the evolved gas and examine its properties.

Experiment 133.—Repeat Experiment 132, using zinc or iron in the place of copper.

Nitrogen Trioxid, N_2O_3

343. Preparation and Properties.—This oxid is formed by the action of starch, sugar, arsenious oxid, and other easily oxidizable bodies upon nitric acid. The reaction is really a complex one giving a mixture of the trioxid and tetroxid from which the pure nitrogen trioxid may be separated. It can also be prepared by the addition of oxygen to the dioxid in the proper proportion. It exists as a blue liquid at low temperatures; as a brown-red gas at high temperatures. At ordinary temperatures the gas seems to be a mixture of NO and NO_2. In ice-cold water it dissolves to a blue liquid forming nitrous acid.

344. Nitrous Acid, HNO_2.—This may be prepared by the method just given.

$$N_2O_3 + H_2O = 2HNO_2.$$
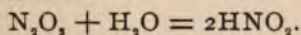
It is known only in solution and is very unstable. It readily decomposes into nitric acid and nitric oxid. Its salts are known as nitrites and are quite stable. They are prepared by the reduction of nitrates, sometimes by simply heating them, or by the oxidation of ammonia. They also occur naturally in the atmosphere, in natural waters and in plant and animal juices. They deflagrate when thrown on hot charcoal and are decomposed by acids with the evolution of red fumes.

$$2KNO_2 + H_2SO_4 = K_2SO_4 + 2HNO_2.$$
$$2HNO_2 = H_2O + N_2O_3 (i. e., NO + NO_2).$$
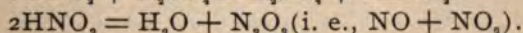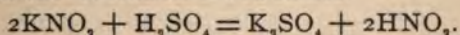
Sodium nitrite is largely used in organic laboratories.

Experiment 134.—Allow air to mix with a test-tube full of nitric oxid formed in Experiment 132, and then immerse the open end of the tube in water; or better, fill a tube with nitric oxid and while over the pneumatic trough allow oxygen from the cylinder to enter, bubble by bubble. Note all changes.

Experiment 135.—Treat a solution of potassium nitrite with an acid. What is evolved?

Nitrogen Peroxid or Tetroxid, N_2O_4 or NO_2

345. Preparation and Properties.—This oxid is formed when nitric oxid comes in contact with the proper equivalent of oxygen. It is also formed by the decomposition of some nitrates as lead nitrate, $Pb(NO_3)_2$, by heat.

$$Pb(NO_3)_2 = N_2O_4 + PbO_2.$$
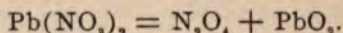
The first form, N_2O_4, is liquid at low temperatures, and a solid at $-20°$. By a slight rise of temperature it is dissociated into NO_2 which is a red-brown gas. At $140°$ the gas consists wholly of NO_2. This is decomposed by solution in water giving nitric and nitrous acids.

$$2NO_2 + H_2O = HNO_2 + HNO_3.$$
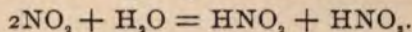
This oxid must therefore be looked upon as a compound of the trioxid and pentoxid. It forms no distinctive hydroxid of its own. It is a powerful oxidizing agent. It does not ordinarily support combustion though phosphorus can be made to burn in it. It is poisonous when breathed.

Nitrogen Pentoxid, N_2O_5

346. Preparation and Properties.—This is prepared by removing water from nitric acid by means of phosphorus pentoxid,

$$2HNO_3 = N_2O_5 + H_2O,$$
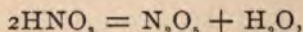
or by the action of chlorin upon silver nitrate,

$$2AgNO_3 + Cl_2 = 2AgCl + N_2O_5 + O.$$
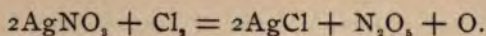
It is a crystalline solid, melting at 30°, decomposing spontaneously, and combining with water with great energy to form nitric acid.

$$N_2O_5 + H_2O = 2HNO_3.$$
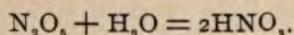
347. Nitric Acid, HNO_3.—This was one of the earliest acids known and was called *aqua fortis*. It can be formed by the action of the electric spark upon moist air and hence is found in the atmosphere after the passage of lightning. This acid may then be washed down to the earth by the rain. It is also formed by the decay of nitrogenous organic matter in the presence of an excess of oxygen and of strong bases. These processes account for the large deposits of nitrates found in various parts of the world, as the potassium nitrate or saltpetre of India, and the sodium nitrate found in Chile. Nitric acid is prepared by acting upon a nitrate, generally sodium nitrate (as the cheapest) with a stronger non-volatile acid, as sulphuric acid.

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$
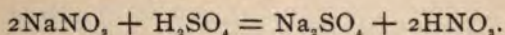
The heating must be gentle as the acid is decomposed by too high a temperature. It is concentrated and purified by redistillation with sulphuric acid and passing air through it in the dark, as it is decomposed by bright light.

348. Properties.—Nitric acid is a colorless liquid, boiling at 86°, and is a solid at —47°. It has a specific gravity of 1.55, fumes in the air and turns yellow in the light and on heating, from a partial decomposition, with separation of the oxids of nitrogen which remain dissolved in the acid. The ordinary commercial acid

has a specific gravity of 1.4 and contains 68 per cent. of nitric acid.

349. Action of Nitric Acid.—When a metal acts upon nitric acid, hydrogen is not evolved, but the hydrogen liberated reacts with more nitric acid with the evolution of nitric oxid, NO. The reaction may be looked upon as taking place in two stages :

$$3Zn + 6HNO_3 = 3Zn(NO_3)_2 + 6H,$$
$$6H + 2HNO_3 = 4H_2O + 2NO,$$

or,

$$3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 4H_2O + 2NO.$$
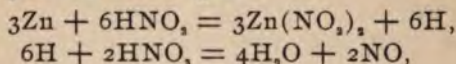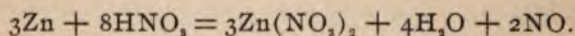
From an oxid we have

$$ZnO + 2HNO_3 = Zn(NO_3)_2 + H_2O.$$
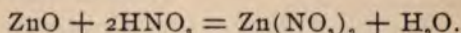
Upon some elements, as tin, it exerts an oxidizing action only, not forming the nitrate nor bringing the metal into solution. It also oxidizes the more negative elements as sulphur, phosphorus, etc. It oxidizes organic matter, attacking the skin and mucous membrane. It is therefore a corrosive poison.

Experiment 136.—Dissolve lead in a mixture of equal parts of concentrated nitric acid and water with heat. What is given off and what crystallizes out on cooling ?

Experiment 137.—Note the action of nitric acid on several metals including antimony or tin. Also on the skin and on a piece of silk or wool.

350. Aqua Regia.—This is a name given to a mixture of concentrated hydrochloric and nitric acids. The proportions are about three parts of the former to one of the latter. It is a solvent for gold (hence the name) and platinum which will not dissolve in either hydrochloric acid or nitric acid alone. Its powerful solvent action is, chiefly at least, due to the formation of chlorin and nitrosyl chlorid.

$$3HCl + HNO_3 = 2H_2O + NOCl + 2Cl.$$
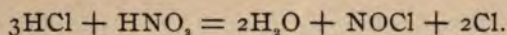
When gold and platinum are dissolved in *aqua regia*, auric chlorid, $AuCl_3$, and platinic chlorid, $PtCl_4$, are formed.

Experiment 138.—Examine the action of *aqua regia* on antimony or tin and compare with the action of each of its constituents taken separately. (For the action of nitric acid see Section 348.)

351. The Nitrates.—Nitric acid is a monobasic acid and its compounds are called nitrates. They are numerous and important. These nitrates are crystalline solids, losing oxygen on being heated and decomposing energetically when heated with oxidizable matter. They deflagrate when heated on charcoal, melt easily and are all soluble in water. Some nitrates of less positive elements, as bismuth, are decomposed by water, forming basic nitrates.

Experiment 139.—Heat a small quantity of sodium nitrate in a test-tube with enough concentrated sulphuric acid to cover it. Note the condensation of nitric acid on the sides of the tube.

352. Sodium Nitrate, $NaNO_3$.—Sodium nitrate is also known as cubic nitre and Chile saltpetre. It is found in large deposits in Chile. It is used to make nitric acid and hence is largely used in the manufacture of sulphuric acid. It is also used for the manufacture of inferior gunpowder and fertilizers.

353. Potassium Nitrate, KNO_3.—This is called nitre and saltpetre. It is found in India. It is formed by the decay of nitrogenous matter in rainless seasons and in sheltered places, as under old houses. This natural process is imitated in artificial nitre plantations where nitrogenous organic matter, wood ashes, porous earth, etc., are heaped up under shelters and allowed to stand through many months. Potassium nitrate is now largely

made, by double decomposition, from potassium chlorid and sodium nitrate.

$$KCl + NaNO_3 = KNO_3 + NaCl.$$
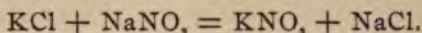
Potassium nitrate is used to make the finer grades of gunpowder and to preserve food.

354. Gunpowder.—Gunpowder consists of an intimate mixture of saltpetre 75 per cent., charcoal 12 to 15 per cent., and sulphur 13 to 10 per cent. The composition varies slightly according to the purpose for which it is to be used. The finely pulverized materials are thoroughly ground together in a moist condition and then pressed in sheets which are broken up and dried, or the moist mass may be pressed in moulds of various sizes and shapes before drying. The force exerted in an explosion of gunpowder is due to the sudden production of a large volume of gas which is greatly expanded by the high temperature generated by the explosion. The principal gaseous products are carbon dioxid, nitrogen, carbon monoxid, and water; the chief solid products (gaseous at the temperature of the explosion) are potassium carbonate, sulphid, and sulphate, and uncombined sulphur.

Experiment 140.—Heat a small piece of potassium nitrate on charcoal before the blowpipe.

Experiment 141.—(Two or three students perform this together.) Weigh six grams of potassium nitrate, one gram of roll sulphur, and one gram of charcoal. Place in a mortar, moisten slightly and grind finely and intimately together. Place in small portions on filter-paper to dry. When dry, test its inflammability.

355. Silver Nitrate, $AgNO_3$.—This substance has been known for a long time. It was called *lapis infernalis*, and lunar caustic. It is the chief salt of silver as well as one of the most important nitrates. It

is prepared by dissolving silver in nitric acid. Silver nitrate cauterizes organic matter, and is poisonous. It is used medicinally. It is easily decomposed by contact with organic matter, as dust or a piece of paper or cloth or the skin. It is therefore used for indelible ink.

356. Other Nitrates.—Calcium nitrate is sometimes formed in nature by the same processes as result in the formation of the alkaline nitrates. It resembles them in general properties. Strontium and barium nitrates are used for fireworks, giving red and green fires respectively· Lead nitrate is one of the most important of the lead salts as it is one of the few compounds of lead which are soluble. It is formed by the action of nitric acid upon lead and is used in the production of other lead compounds. Basic nitrates are formed by mercury, bismuth, iron, and some other elements. These are not all soluble. The basic nitrate of bismuth (bismuth subnitrate) is used as a cosmetic and as a medicine.

357. Nitrogen Sulphids.—So far as known, nitrogen forms only one sulphid, N_4S_4.

358. Phosphorus Oxids.—Phosphorus forms several oxids. The two typical oxids, the trioxid, P_2O_3, and the pentoxid P_2O_5, are the most important.

Phosphorus Trioxid, P_2O_3

359. Preparation and Properties.—This is formed by the slow oxidation of phosphorus at a low temperature or in a limited amount of oxygen or air. It is a crystalline solid, melting at 23°. It is decomposed at 300° and in contact with oxygen it is oxidized to phosphorus pentoxid, P_2O_5. It has a garlic-like odor and combines readily with water, forming phosphorous acid.

$$P_2O_3 + 3H_2O = 2H_3PO_3.$$
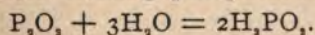
360. Phosphorous Acid, H_3PO_3.—This acid is best formed by the decomposition of phosphorus trichlorid by means of water.

$$PCl_3 + 3H_2O = P(OH)_3 + 3HCl.$$
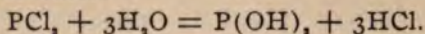
It is a solid, deliquescing into a thick syrup which absorbs oxygen from the air and becomes phosphoric acid. On being heated, it decomposes into phosphoric acid and phosphin. It is a strong reducing agent. It is a dibasic acid with the probable constitution

$$O{=}P{\diagup}{\overset{OH}{\underset{H}{\diagdown}}}{-}OH.$$ Its compounds are called phosphites.
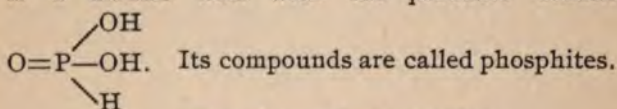
Phosphorus Pentoxid, P_2O_5,

361. Preparation and Properties.—This oxid is formed when phosphorus is burned at a high temperature or in the presence of an excess of oxygen. It is a flaky powder, sometimes crystalline, volatile at 250°, but dissociated at a higher heat. It greedily absorbs water, having a greater affinity for water than is shown by any other body. This makes it useful for removing water from other substances. This union with water forms an acid.

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$
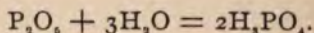
362. Phosphoric Acids.—There are three phosphoric acids. Orthophosphoric acid is formed by oxidizing phosphorus with nitric acid. It is a crystalline solid, very soluble in water. It is usually seen in solution in water. Its compounds with the bases are called phosphates. Its constitution may be represented as follows:

$$O{=}P{\diagup}{\overset{OH}{\underset{OH}{\diagdown}}}{-}OH.$$ When raised to a red heat it loses water
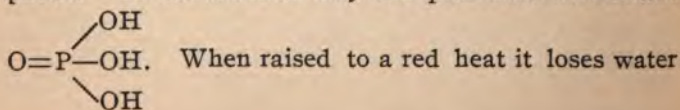
and is changed into metaphosphoric acid, HPO, or

HO—P$\langle^O_O$. This is commercially called glacial phos-

phoric acid. The compounds of this acid are called meta-phosphates. Between these two acids lies the pyrophos-

phoric acid, $H_4P_2O_7$, or $\begin{matrix} HO \\ HO \end{matrix}\rangle P\langle^O_{} \\ \begin{matrix} HO \\ HO \end{matrix}\rangle P\langle^O_O$ formed by a more

gentle heating of orthophosphoric acid. Its salts are the pyrophosphates. Of these three acids, orthophos-phoric acid is the most important. Its compounds are numerous and useful. Regarding these acids as derived from phosphorus pentoxid, the ortho acid is formed from one molecule of the pentoxid and three molecules of water ; the pyro acid from one molecule of the pentoxid and two molecules of water ; the meta acid from one molecule of the pentoxid and one molecule of water.

363. Basicity of the Phosphoric Acids.—Orthophos-phoric acid is tribasic and forms three classes of salts according as one, two, or three of the hydrogens in the hydroxyls are replaced by their equivalents of a positive element, thus :

Na_3PO_4, trisodium phosphate or normal sodium phosphate.

Na_2HPO_4, hydrogen disodium phosphate.

NaH_2PO_4, dihydrogen sodium phosphate.

Metaphosphoric acid is monobasic, though this acid can exist in polymeric forms, and five distinct modifica-tions of metaphosphates are known, thus:
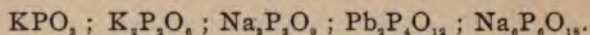
KPO_3 ; $K_2P_2O_6$; $Na_3P_3O_9$; $Pb_2P_4O_{12}$; $Na_6P_6O_{18}$.
Pyrophosphoric acid is tetrabasic.

364. Phosphates.—Some of these, as the calcium and magnesium phosphates, are found widely distributed. A number of others are found more rarely and in smaller quantities. Certain of them are found in plants and animals. The alkaline phosphates are soluble, the others are with difficulty so, or are insoluble. They are stable, crystallize well and are very useful to plants and animals. Double phosphates are easily formed.

PHOSPHATES OF GROUP I

Among the phosphates of Group I, sodium phosphate is the most important. This is the disodium hydrogen phosphate, Na_2HPO_4. It is a white crystalline salt and is soluble in water. Though what is called an acid salt, it is alkaline to litmus, as are the hydrogen alkaline carbonates. A sodium and ammonium phosphate, $NaNH_4HPO_4.4H_2O$, occurs in urine. Much importance was attached to this salt in early times and it was called microcosmic salt. It is also known as salt of phosphorus and is used in blowpipe analysis. Other ammonium phosphates are found in urine.

365. Calcium Phosphates.—The most important of all the phosphates is the tricalcium or bone phosphate, $Ca_3(PO_4)_2$. It is the chief constituent of bones in which it is accompanied by a small amount of magnesium phosphate. It is also found in a number of minerals as phosphorite, apatite, phosphate rock, etc. It is in all fertile soils and from them is taken up by plants. It is one of the chief fertilizing agents used.

By treatment with an acid this bone phosphate is changed into " soluble phosphate."

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$
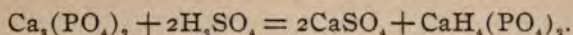
This is soluble in water and is easily assimilated by the plants. Another salt of phosphoric acid occurring in fertilizers is the "reverted" or "precipitated" phosphate, $CaHPO_4$. This is not soluble in water but is easily dissolved by dilute acids and by certain salts of ammonium. It is supposed to be soluble in the juices of plants, and so readily assimilable by them. Tricalcium phosphate can be dissolved only by strong acids. Phosphates of iron and aluminum occur naturally. They are insoluble in water. They may prove an important source of phosphoric acid.

Experiment 142.—Make a bead of microcosmic salt on a loop of platinum wire and dissolve in it, when fused, some metallic oxid as that of cobalt or chromium. Use any salts of these metals. Compare with the borax bead (Experiment 118).

Experiment 143.—To a solution of magnesium sulphate add ammonium chlorid and then ammonium hydroxid until it smells of ammonia. Then add a solution of disodium phosphate. What is formed? What is the character of the precipitate?

366. Hypophosphorous Acid, H_3PO_2.—The salts of this acid are formed by decomposing phosphids of Group II with water or by boiling phosphorus and water with a hydroxid of Group I or II.

$$3Ba(OH)_2 + 8P + 6H_2O = 3Ba(PH_2O_2)_2 + 2PH_3.$$
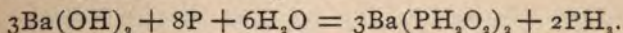
The acid can be obtained by adding sulphuric acid to barium hypophosphite. It is a white crystalline mass which decomposes on being heated, forming phosphin. It has a strong reducing action. Most hypophosphites are soluble in water. They do not alter in the air when dry. They show a reducing action and are used medicinally.

Hypophosphorous acid acts as a monobasic acid, only one of its hydrogen atoms being replaceable by a posi-

tive element, hence it seems to have but one hydroxyl

group and its constitution is thought to be $O{=}P{<}^{OH}_{H}$.

367. Phosphorus Sulphids.—The most important sulphid of phosphorus is phosphorus pentasulphid, P_2S_5, corresponding to P_2O_5. This is used largely in organic laboratories for forming thio-compounds.

368. Arsenic Oxids.—Arsenic forms several oxids. Two of these are important, the trioxid, As_2O_3, and the pentoxid, As_2O_5, following the typical oxids of the group.

Arsenic Trioxid, As_2O_3

369. Preparation and Properties.—Arsenic trioxid is also known as arsenious oxid. It is found free though not abundantly. It is prepared by roasting arsenic ores in the air. The white powder obtained is known as white arsenic, poison flour, etc. "Arsenic glass" is formed by melting this powder. It is hard and vitreous but on standing a while it changes to "arsenic porcelain," becoming opaque and white. It is heavy (specific gravity 3.7), has no smell, but a slight sweetish metallic taste, melts at 200°, and crystallizes in regular octahedra on cooling. Arsenic trioxid is slightly soluble in water, forming a solution which acts as if it contained the acid, H_3AsO_3, having a faint acid reaction and combining with strong bases. This oxid also dissolves in hydrochloric acid forming a chlorid and thus acting as a base.

Arsenic trioxid is used for fining glass and in the preparation of other arsenic compounds. Its poisonous qualities make it useful as an insecticide. It is a very poisonous body.

370. Arsenites.—While the existence of arsenious acid, H_3AsO_3, is hypothetical, a number of arsenites or salts of this acid are known. These are very poisonous. The alkaline arsenites are soluble in water. They crystallize poorly and are deliquescent. Copper arsenite $Cu_3(AsO_3)_2$, is a bright green salt, known as Scheele's green and used as a pigment, though it is poisonous and should not be so used. A more largely used pigment is Paris green (Schweinfurt green, or emerald green). This is a double arsenite and acetate of copper, $Cu_3(AsO_3)_2.Cu(C_2H_3O_2)_2$, and is formed by boiling together white arsenic and verdigris.

Experiment 144.—Burn a little arsenic oncharcoal.

Experiment 145.—Boil arsenic trioxid with water and test the solution with litmus paper. Treat the solution with hydrogen sulphid and then acidify with hydrochloric acid.

Experiment 146.—Dissolve arsenic trioxid in sodium hydroxid. What is formed?

Arsenic Pentoxid, As_2O_5

371. Preparation and Properties.—Arsenic pentoxid does not occur in nature but is formed by oxidizing the element or the trioxid with nitric acid. This gives first the hydroxid, $AsO(OH)_3$, which on being heated loses water and leaves arsenic pentoxid, As_2O_5. This pentoxid is a white mass, deliquescent, melting when heated, and decomposing into arsenic trioxid and oxygen.

372. Arsenic Acids.—The preparation of the hydroxid has been given above. This is orthoarsenic acid corresponding to orthophosphoric acid and coming from the union of arsenic pentoxid and three molecules of water. It is a crystalline solid with an unpleasant taste, acting as a caustic upon the skin and other organic matter. It is not as poisonous as arsenic trioxid. With

bases it combines forming arsenates. Heated to 180° water is lost and pyroarsenic acid, $H_4As_2O_7$, is left; heated to 200° a further molecule of water is lost and metarsenic acid, $HAsO_3$, is left. The relation between these acids is the same as between the phosphoric acids. The arsenates are isomorphous with and analogous to the phosphates. They crystallize better than the arsenites. Some of the arsenates are used in calico-printing. They are not so poisonous as the arsenites. The pentoxid is also used for oxidizing purposes, as in the preparation of anilin dyes.

Experiment 147.—To a solution of magnesium sulphate add ammonium chlorid and then ammonium hydroxid until it smells strongly of ammonia. Then add a solution of disodium arsenate. Compare the precipitate with that obtained in Experiment 143.

Experiment 148.—Oxidize arsenic trioxid with nitric acid. What is given off? What is formed? Neutralize the solution with ammonium hydroxid and test with copper sulphate solution.

373. Arsenic Sulphids.—Arsenic forms three sulphids. The disulphid, As_2S_2, realgar, occurs in nature. The trisulphid, As_2S_3, and the pentasulphid, As_2S_5, corresponding to the two oxids are formed by precipitating solutions of arsenites and arsenates respectively with hydrogen sulphid. Both are yellow. The trisulphid occurs in nature and is called orpiment.

The hydrosulphids of arsenic are unstable, but form a series of salts, the thioarsenites and thioarsenates, corresponding to the arsenites and arsenates; as Na_3AsS_3 and Na_3AsS_4. When treated with acids these decompose with the evolution of hydrogen sulphid and the precipitation of the sulphid.

374. Antimony Oxids.—Several oxids are formed by antimony. There are two typical oxids, antimony trioxid, Sb_2O_3, and pentoxid, Sb_2O_5, and then a third

oxid, antimony tetroxid, Sb_2O_4. Similar tetroxids are known for phosphorus and arsenic but are not important enough for separate mention.

Antimony Trioxid, Sb_2O_3

375. Preparation and Properties.—This oxid occurs free. It is formed by burning antimony in the air. It is a white powder nearly insoluble in water. On being heated in the air it changes to the tetroxid. It dissolves in alkaline hydroxid giving salts which are called metantimonites.

$$Sb_2O_3 + 2KOH = 2SbO_2K + H_2O.$$
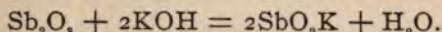
With strong acids it acts as a base, giving salts of antimony. There is a tendency to the formation of basic salts.

Antimony trioxid forms two hydroxids, $Sb(OH)_3$, or orthoantimonious acid, and $Sb_2O(OH)_4$, which might be called pyroantimonious acid. The antimonites are of little interest. The salts of antimony in which the element acts the part of a base (is positive to some acid radical) are of considerable importance. The chlorid, or butter of antimony, and the double tartrate of potassium and antimony, or tartar emetic, are the most important.

Antimony Tetroxid, Sb_2O_4

376. Preparation and Properties.—This oxid is formed by highly heating either of the other oxids and therefore seems to be the most stable oxid under the influence of heat and oxygen. It is neutral, insoluble in water, and forms no hydroxid nor other compound.

Antimony Pentoxid, Sb_2O_5

377. Preparation and Properties.—Antimony pent-

oxid, Sb_4O5, is prepared by oxidizing the element or its trioxidvery strongly. It is a yellowish powder, is insoluble and loses oxygen on being heated. Three hydroxids can be prepared : orthoantimonic acid, H_3SbO_4, pyroantimonic acid, $H_4Sb_2O_7$, and metantimonic acid, $HSbO_3$. These show the analogy to phosphorus and arsenic but are of theoretical interest only. A few salts are known.

378. Antimony Sulphids.—Antimony forms two sulphids, the trisulphid, Sb_2S_3, and the pentasulphid, Sb_2S_5, corresponding to the oxids. The trisulphid is also known as stibnite and is the most abundant compound of antimony in nature. The natural trisulphid is black, the artificial is orange-red. The hydrosulphids are analogous to those of arsenic and tin.

379. Bismuth Oxids.—Bismuth forms four oxids, three of which correspond to those of antimony, the trioxid, Bi_2O_3, pentoxid Bi_2O_5, and tetroxid, Bi_2O_4. A fourth oxid is known as bismuth monoxid, BiO, and is a brownish powder, oxidizing very readily and acting as a base.

Bismuth Trioxid, Bi_2O_3

380. Preparation and Properties.—This occurs in nature. It is prepared by burning bismuth or by heating its hydroxid, $Bi(OH)_3$, which may be prepared by adding an alkaline hydroxid to a solution of bismuth salt. It is a yellow powder, insoluble and base-forming. The salts are decomposed by water, forming basic salts. The most important of these salts are the basic nitrate and basic carbonate called commercially subnitrate and subcarbonate. These are used medicinally and as cosmetics. They are white insoluble powders.

Bismuth Pentoxid, Bi_2O_5

381. Preparation and Properties.—This oxid is prepared by heating the hydroxid, $HBiO_3$, which is formed by passing a current of chlorin through a boiling solution of potassium hydroxid, holding bismuth trioxid in suspension. Bismuth pentoxid is very unstable. It has one hydroxid which has just been mentioned. This hydroxid, which is sometimes called metabismuthic acid, forms no salts. It is important to note the diminution in acid properties in the pentoxids of this group as the atomic weight increases.

382. Bismuth Sulphids.—Bismuth forms two sulphids, bismuth sulphid, BiS, and bismuth trisulphid, Bi_2S_3. The latter is found in nature, while the former is prepared by precipitation from a solution of a bismuth salt with hydrogen sulphid.

OXIDS OF THE POSITIVE SERIES OF GROUP V

Vanadium forms five oxids corresponding to those of the group element. Some of these form basic hydroxids and others acid hydroxids. The pentoxid is the most important, giving two acids, metavanadic, HVO_3, and pyrovanadic, $H_4V_2O_7$. The vanadates are numerous, some of them occurring in nature. They are so rare that there can be as yet little technical interest attaching to them.

For columbium and tantalum, the chief oxids are the pentoxids giving columbic acid, $HCbO_3$, and tantalic acid, $HTaO_3$. These form numerous and complex columbates and tantalates, some of which occur naturally.

THE OXIDS OF GROUP VI

383. General Characteristics.—These are of the types

MO_2 and MO_3, and are acid-forming. Not infrequently other oxids are known. Ozone would correspond to the type OO_2.

384. Sulphur Oxids.—Sulphur forms several oxids but the typical ones, sulphur dioxid SO_2, and sulphur trioxid, SO_3, are the only ones of importance.

Sulphur Dioxid, SO_2

385. Preparation and Properties.—Sulphur dioxid occurs in the fumes coming from volcanoes. It is formed whenever sulphur is burned in the air or in oxygen. It is also obtained by the action of metals as copper or mercury on hot concentrated sulphuric acid.

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2.$$
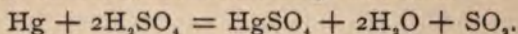
386. Properties.—It is a colorless gas with a suffocating smell. It is more than twice as heavy as air, having a specific gravity of 2.2. Sulphur dioxid is quite soluble in water, forming sulphurous acid. It does not burn nor support combustion, and is condensed by pressure and cold to a colorless liquid. It bleaches organic coloring-matter and acts as a disinfectant. These actions are observed only in the presence of water. They are therefore more properly to be considered as properties of the hydroxid or sulphurous acid.

Experiment 149.—Form sulphur dioxid (*a*) by burning sulphur; (*b*) by treating sodium sulphite with sulphuric acid; (*c*) by the action of copper on hot concentrated sulphuric acid.

387. Sulphurous Acid, H_2SO_3.—This acid is formed by the solution of the dioxid in water.

$$SO_2 + H_2O = H_2SO_3.$$
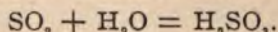
Sulphurous acid is known only in solution. The solution oxidizes on standing and is decomposed by light. It is a dibasic acid and forms two classes of sulphites, normal sul-

phites in which both hydrogen atoms are substituted by a positive element, and bisulphites or acid sulphites where only one atom is thus substituted. The constitution of the

acid is probably $\begin{array}{c} O \\ O \end{array} \Big\rangle S \Big\langle \begin{array}{c} H \\ OH \end{array}$.

Sulphurous acid is a weak acid and when the sulphites are treated with a strong acid, sulphurous acid is liberated and readily breaks up into sulphur dioxid and water.

388. The Sulphites.—The sulphites are numerous and useful. The bisulphites of sodium, magnesium, and calcium are used in the preparation of wood-pulp for paper. These bisulphites are deliquescent and very soluble bodies. The normal sulphites are more easily crystallized and less soluble. Sodium and calcium sulphites are the most important commercially. Some sulphites are used medicinally. The sulphites are strong reducing agents. They are sometimes used for bleaching purposes and in photography. Sulphurous acid is itself a valuable bleaching and reducing agent, and is largely used for bleaching woolens, silks, and straw goods.

Sulphur Trioxid, SO_3

389. Preparation.—This oxid cannot be formed by the direct burning of sulphur. Sulphur dioxid, however, can be made to take up an additional atom of oxygen by passing the two gases over heated platinum sponge.

$$SO_2 + O = SO_3$$
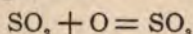
Or the dioxid will take oxygen from the oxids of nitrogen.

$$SO_2 + N_2O_3 = SO_3 + 2NO.$$
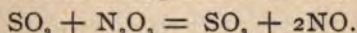
This reaction will take place at ordinary temperatures.

Sulphur trioxid is generally obtained for experimental purposes by heating fuming sulphuric acid.

$$H_2SO_4.SO_2 = SO_2 + H_2SO_4.$$
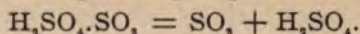
390. Properties.—Sulphur trioxid is a colorless liquid, crystallizing in long fine white needles when cooled, and dissociated at a red heat. With a small portion of water it forms a solid crystalline product at ordinary temperatures. It absorbs water with great readiness, dissolving in it with the evolution of great heat.

Sulphuric Acid, H_2SO_4

391. Preparation.—This is the most important and useful of the acids. It has been found free in a few rivers and lake waters, usually of volcanic origin. It is prepared in leaden chambers of large size by the interaction of sulphur dioxid, water, the oxids of nitrogen, and air:

$$SO_2 + H_2O + N_2O_3 = H_2SO_4 + 2NO.$$
$$2NO + O = N_2O_2.$$
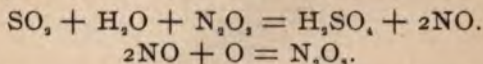
The nitrogen trioxid is thus regenerated and theoretically a small amount would suffice for the production of an indefinite amount of sulphuric acid.

These equations are not to be taken as expressing in full the reactions which take place. It is probable that the true reactions are more complex giving intermediate products. The nature of these is a matter of dispute. They depend upon the temperature, amount of water, and possibly other conditions. It has been maintained that a solid compound, $SO_2\begin{subarray}{l} \diagup NO_2 \\ \diagdown OH \end{subarray}$, called lead chamber crystals, is the chief intermediate compound and that this is decomposed by the addition of water into sulphuric acid, nitric acid, and nitric oxid.

Fig. 35.
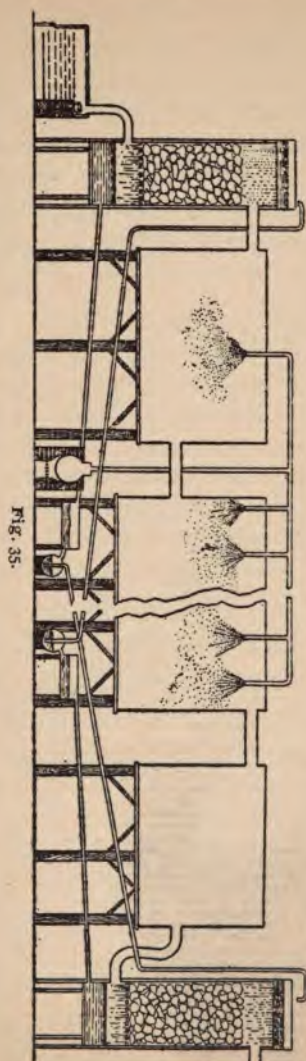
Large chambers of lead (with a capacity of 100,000 cubic feet or more) are used in carrying out the process. These are connected by leaden passages. The sulphur dioxid is obtained by burning sulphur or a metallic sulphid (iron pyrites). This sweeps air and the vapors of nitric acid or oxids of nitrogen along with it into the chambers. Steam enters through jets into the chambers. The sulphuric acid formed collects on the bottom of the chambers.

392. Properties.—The sulphuric acid coming from these chambers, called chamber acid, contains a good deal of water. It must be concentrated by heating in leaden pans and then finally distilling from platinum or glass. It is a colorless oily liquid with a specific gravity of 1.85. It mixes with water in all proportions evolving great heat and also contracting in volume. This affinity for water is very noteworthy. It will remove water from gases and so can be used for drying them. It removes water from organic matter, leaving the carbon, and so charring it. Thus it causes very painful wounds upon the flesh, having a violently corrosive action. In the concentrated form it is a corrosive poison. The constitutional formula for sulphuric acid is

$$O{\Large\diagdown}\atop O{\Large\diagup}{\Large S}{{\diagup}^{OH}_{\diagdown OH}}$$

393. Sulphates.—While the dilute acid has a considerable solvent action upon a number of metals, the cold concentrated acid has little action. This is in part due to the insolubility of the sulphate formed in the concentrated acid. The compounds of sulphuric acid are called sulphates and they form a large and important class of salts. The acid is dibasic like sulphurous acid. The bisulphates are deliquescent and very soluble in water. They are far less important than the sulphates

and can usually be transformed into them by heating. Many of the sulphates occur in great abundance naturally. Most of them crystallize well and are soluble in water. The insoluble ones are those of the first series, Group II, and lead. The sulphates can be formed (*a*) by the action of sulphuric acid upon the oxids or carbonates of the elements or upon the metals, and (*b*) often by roasting the sulphids. In the case of the insoluble ones they can be obtained by precipitation with a soluble sulphate.

Experiment 150.—Dissolve iron in sulphuric acid and evaporate the solution nearly to dryness, allowing it to crystallize. Repeat with ferrous sulphid in the place of iron. What is formed and what is evolved?

Experiment 151.—Let concentrated nitric acid act upon lead sulphid (galena). Lead sulphate is insoluble. What is formed?

Experiment 152.—Treat barium chlorid with sulphuric acid, with sodium sulphate, and with ferrous sulphate. What is formed in each instance?

SULPHATES OF GROUP I

These are generally white soluble crystalline solids, though copper sulphate is blue. They are very stable.

394. Sodium Sulphate, $Na_2SO_4.10H_2O$, is known also as Glauber's salt or *sal mirabile*. It is very widely distributed in nature, especially in solution in various mineral waters. It is made in the Le Blanc process for manufacturing sodium carbonate and is there called salt cake. It is used medicinally and for glass-making.

395. Potassium Sulphate, K_2SO_4, is found in the salt beds at Stassfurt. It is largely used as a fertilizer under the name kainite, and also for making alum. It is, like the sodium salt, white, crystalline, and soluble in water. Ammonium sulphate, $(NH_4)_2SO_4$, is similar to

the potassium salt and is also used as a fertilizer, and for making alum. Potassium bisulphate, $KHSO_4$, is a deliquescent white solid, decomposing on being heated to a high temperature. It is used as a flux in fusing and decomposing minerals.

396. Copper Sulphate, $CuSO_4.5H_2O$, is known as bluestone. It loses water on heating and becomes white. On heating higher it is changed to copper oxid and the sulphuric acid is volatilized. It was called in early times blue vitriol. It is found in small amount in nature. It is soluble in water and is poisonous. It is used in electroplating, dyeing, and as an insecticide.

Sulphates of Group II

397. Magnesium Sulphate, $MgSO_4.7H_2O$, is known as Epsom salts. It is found dissolved in a great many natural waters, and is a white crystalline soluble body. Large quantities of it are obtained from the German salt beds. It is used medicinally.

398. Calcium Sulphate, $CaSO_4.2H_2O$, is very widely distributed and abundant. It is known under a number of different names, as gypsum, plaster, alabaster, etc. When it occurs free of water it is called anhydrite. When the water is driven off by heating or "burning" it is called "plaster of Paris" and is capable of reabsorbing water and "setting" or hardening. This form is largely used as a cement and for taking casts of objects. The ground gypsum, or "land plaster," is largely used as a fertilizer. Calcium sulphate is prepared artificially by precipitation with an alkaline sulphate and is then a white powder, only slightly soluble in water. When gypsum is dissolved in natural waters these are said to be permanently hard, as it cannot be removed by any of

the simple means adopted for the removal of calcium carbonate, which renders the water temporarily hard.

399. Barium Sulphate, $BaSO_4$, occurs in hard crystalline masses and is called heavy spar on account of its high specific gravity. It is also called barite. This is ground to a powder and is used as an addition to paint, paper, etc. Prepared artificially by precipitation it is a heavy, white, and very insoluble powder.

400. Zinc Sulphate, $ZnSO_4.2H_2O$, is known as white vitriol. It is prepared in some forms of galvanic batteries. It is a poisonous body, soluble in water, and crystallizing with water of crystallization.

401. Mercuric Sulphate, $HgSO_4$, is a white soluble crystalline body used in some batteries.

SULPHATES OF GROUP III

402. Aluminum Sulphate, $Al_2(SO_4)_3$, is the principal compound of aluminum. It is white and very soluble in water. It is not easy to crystallize and keep from absorbing water and hence is not so much used in this form. It is decomposed by heating.

403. Alums.—Aluminum sulphate very readily forms double sulphates, combining with the sulphates of the univalent elements. These double sulphates are known as alums. Thus, with potassium sulphate, potassium alum is formed: $Al_2(SO_4)_3.K_2SO_4.24H_2O$ or $KAl(SO_4)_2.12H_2O$.

The term alum has been extended to all double sulphates of a trivalent and univalent element. The trivalent element may be Al, Fe, Cr, etc. ; the univalent element may be Na, K, Rb, Cs, Tl, Ag, or NH_4, or an organic derivative of ammonia. Except in the case of aluminum, the name of the trivalent element is added to designate the alum.

404. Preparation of Alums.—Potassium alum occurs in nature and has been used for a long time. A pure form of it is known as Roman alum. Potassium alum is found dissolved in alum waters. It may be made from alum shales (aluminum silicates containing considerable amounts of iron pyrites, FeS_2) by roasting so as to form aluminum sulphate and ferrous sulphate. These are dissolved in water, the ferrous sulphate crystallized out, potassium sulphate added, and the alum crystallized out. Or by adding ammonium sulphate, ammonium alum is obtained. Sodium alum is not manufactured as it is very deliquescent.

Experiment 153.—Dissolve aluminum sulphate in a small quantity of water and divide the solution into two portions. To one add a solution of potassium sulphate and set both away to crystallize. Which crystallizes the better?

405. Properties of the Alums.—Potassium (or ammonium) alum crystallizes readily and does not absorb water. It is accordingly used in the place of aluminum sulphate, the presence of the alkaline sulphate not being objectionable. The alums are used medicinally, in tanning, and, as mordants, in dyeing. When coloring-matters are precipitated with alum, lake dyes are obtained. Alum is also used in purifying water for drinking purposes. As small amounts of alum interfere with the digestive processes it must be used carefully when in connection with water and food. Alum is an astringent. It is efflorescent, losing water on exposure to the air.

406. Other Sulphates.—The remaining useful sulphates may be spoken of together. Lead sulphate, $PbSO_4$, is white and very insoluble. It is used as a paint. In cases of lead poisoning a soluble sulphate is

administered so as to precipitate the lead in the system in the form of the insoluble sulphate. Chromium sulphate, $Cr_2(SO_4)_3$, resembles aluminum sulphate in its properties and uses. It forms alums or double sulphates with the alkaline sulphates. It is a violet substance.

Ferrous sulphate, $FeSO_4.7H_2O$ (copperas, green vitriol), is the most important salt of iron. It is green, crystalline, soluble in water, and poisonous. Like all of the sulphates of the heavier metals it is decomposed by heating. From it was distilled what was first called oil of vitriol and is now known as fuming sulphuric acid. It is used medicinally and as a disinfectant. It is more properly a deodorant than disinfectant. It is used in tanning, dyeing, ink-making, etc. Ferric sulphate, $Fe_2(SO_4)_3$, is a deliquescent yellowish solid, used medicinally.

407. Other Double Sulphates.—Ferrous sulphate, $FeSO_4$, as well as the sulphates of other bivalent positive elements as Mn, Co, Ni, Mg, etc., form double salts with the sulphates of the alkali metals after the formula $M'_2M''(SO_4)_2.6H_2O$. These salts crystallize well, forming monoclinic tables.

Experiment 154.—Dissolve a small piece of iron in dilute sulphuric acid ; after evaporating somewhat divide the solution and to one portion add a solution of ammonium sulphate and set both away to crystallize. Which crystallizes the better ?

408. Fuming Sulphuric Acid, $H_2S_2O_7$.—This acid is prepared by distilling ferrous sulphate. It fumes in the air ; from this its name is derived. It is used to dissolve indigo and in the making of certain dye-stuffs. It is also called pyrosulphuric acid.

409. Thiosulphuric Acid, $H_2S_2O_3$.—This acid was formerly known as hyposulphurous acid. It has not

been isolated but is seen only in its salts. These are called thiosulphates or hyposulphites. When treated with an acid the thiosulphates are decomposed into water, sulphur dioxid, and sulphur, the latter forming a precipitate. The most important of these thiosulphates is sodium thiosulphate, $Na_2S_2O_3$, which is prepared by boiling sodium sulphite, Na_2SO_3, with sulphur. This has strong reducing powers and is used on that account. It also dissolves certain silver salts, combining with them. It is largely used in photography in the fixing bath under the name of " hypo."

Experiment 155.—Dissolve a little sodium thiosulphate in water and add hydrochloric acid. Note the gases evolved and the precipitate formed.

Experiment 156.—To a solution of silver nitrate add hydrochloric acid. Pour off the supernatant liquid from the precipitate and wash by decantation. Treat the precipitate with sodium thiosulphate and note the action.

410. Thionic Acids.—There is a series of these acids differing by an atom of sulphur; $H_2S_2O_6$, $H_2S_3O_6$, $H_2S_4O_6$, $H_2S_5O_6$. These are called dithionic, trithionic, tetrathionic, and pentathionic acids and form salts which are known as dithionates, etc.

411. Hyposulphurous Acid, H_2SO_2.—This is formed by the reduction of sulphurous acid, H_2SO_3. Its salts are the real hyposulphites, but little is known of them.

412. Selenium Oxids.—Selenium forms two oxids corresponding to the typical oxids, selenious oxid, SeO_2, and selenic oxid, SeO_3. There are also two hydroxids or acids formed, selenious acid, H_2SeO_3, and selenic acid, H_2SeO_4.

Selenium Dioxid, SeO_2

413. Preparation and Properties.—This oxid is pre-

pared by the burning of selenium. It forms white crystals, volatilizing at 300°. It has a peculiar disagreeable odor and is deliquescent. The hydroxid, $SeO(OH)_2$, or selenious acid, H_2SeO_3, is prepared by oxidizing selenium with nitric acid. It is readily reduced yielding selenium. It is a dibasic acid and its compounds are known as selenites. The alkaline selenites are the only ones soluble in water. These selenites are also easily reduced. Heated on charcoal they give the odor of decaying horse-radish.

Selenic Acid, H_2SeO_4

414. Preparation and Properties.—Selenium trioxid, SeO_3, is but little known. The corresponding hydroxid, called selenic acid, H_2SeO_4, is analogous to sulphuric acid and is prepared by the strong oxidation of selenium.

$$Se + 3Cl_2 + 4H_2O = H_2SeO_4 + 6HCl.$$
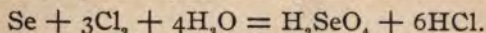
This acid cannot be entirely freed from water. It decomposes at 280° into oxygen and selenious acid. It is a colorless, very acid liquid and not easily reduced. The selenates are analogous to the sulphates.

415. Tellurium Oxids.—Tellurium follows closely the analogy of the preceding elements. It also has two acid-forming oxids. Tellurium dioxid, TeO_2, and tellurium trioxid, TeO_3, from which tellurous and telluric acids respectively are derived.

Tellurium Dioxid, TeO_2

416. Preparation and Properties.—Tellurium dioxid occurs in nature. It is formed by burning tellurium or oxidizing it with nitric acid. It is very slightly soluble in water and melts and boils without decomposition. It is acid-forming and also forms an unstable base. Tel-

lurous acid, H_2TeO_3, is a light white powder, slightly soluble in water and forming a class of salts called tellurites.

Tellurium Trioxid, TeO_3

417. Preparation and Properties.— This oxid is obtained by heating telluric acid. It is a yellow crystalline mass which is decomposed when strongly heated. Telluric acid, H_2TeO_4, is prepared by fusing tellurium, or tellurium trioxid, with potassium carbonate and nitrate and setting free the acid by means of a stronger one.

OXIDS OF THE POSITIVE SERIES OF GROUP VI

418. Chromium Oxids.—Chromium has two base-forming oxids, chromous oxid, CrO, and chromic oxid, Cr_2O_3; and one acid-forming oxid, chromium trioxid, CrO_3.

Chromium Monoxid, Chromous Oxid, CrO

419. Properties.—This oxid is not known free from water. The hydroxid, $Cr(OH)_2$, is prepared by precipitation with a soluble hydroxid. It readily oxidizes to the higher hydroxid. The chromous salts are obtained by reduction from the chromic, generally by heating in hydrogen. They absorb oxygen and change back to basic chromic salts.

Chromium Sesquioxid, Chromic Oxid, Cr_2O_3

420. Preparation and Properties.—This oxid is generally known as chromic oxid. It is found in chrome iron ore. It is prepared artificially by heating the hydroxid. It is a green powder, crystalline, heavy, almost insoluble in acids and is used in coloring glass and porcelain and as a pigment. Several hydroxids are

formed. A series of salts called chromites in which this oxid acts as an acid, has been prepared. Towards strong acids it acts as a base, giving a class of salts called the chromic salts. These are stable towards oxygen, purple or violet colored and the chief of them is the sulphate, $Cr_2(SO_4)_3$, which forms alums and is used in dyeing and tanning. They are easily changed by heating their solutions into green basic salts.

Chromium Trioxid, CrO_3

421. Preparation and Properties.—This is prepared by heating chromium sesquioxid, Cr_2O_3, with an oxidizing agent such as potassium nitrate. An alkaline chromate is thus obtained which can be decomposed by sulphuric acid and the trioxid crystallized out. It crystallizes in long red needles. On being heated, these melt into a red liquid which at 250° is decomposed into the sesquioxid and oxygen. It is easily reduced to the same oxid, Cr_2O_3, by means of organic matter and reducing agents. In fact it has a very powerful oxidizing action upon organic matter. The aqueous solution is often used as an oxidizing agent. The crystals are deliquescent. The solution dyes skin, silk, and wool, yellow. It tastes acid and astringent. It is called chromic acid and gives an important class of salts called chromates.

422. The Chromates.—The generic formula is M_2CrO_4,

or $\begin{array}{c} MO \\ MO \end{array} \diagdown Cr \diagup \begin{array}{c} O \\ O \end{array}$. These and the bichromates are the

most important compounds of chromium. They are the first prepared from the ore and are used in the preparation of all the others. The powdered chromic iron or chromite, is mixed with a carbonate of the first or second group and with some oxidizing material, as potas-

sium nitrate or sodium nitrate, and heated in a furnace. Thus a chromate is formed which can be leached out. These chromates are crystalline, colored, and generally soluble in water. Potassium chromate is one of the most important. It is yellow, soluble, and is decomposed by strong acids forming the bichromate.

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$
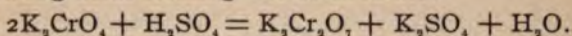
Potassium bichromate, $K_2Cr_2O_7$, is deep red in color and is soluble. The chromates and bichromates are used in preparing dyes and pigments. The most important of these is lead chromate, $PbCrO_4$, which is insoluble and is used as a yellow pigment. The bichromates are also used in photography and in galvanic batteries. It is possible to remove more of the potassium by means of acids forming polychromates. If an excess of acid is added to a chromate and at the same time an oxidizable body, as alcohol, be present, the positive element is separated from the chromic acid, and as this is set free it is reduced by the alcohol and then brought into combination with the excess of acid present and so a salt of chromium obtained. In this way the chromic salts can be prepared.

$$H_2SO_4 + K_2CrO_4 = K_2SO_4 + CrO_3 + H_2O.$$
$$\underset{\text{Alcohol.}}{2CrO_3 + 3C_2H_6O} = \underset{\text{Aldehyde.}}{Cr_2O_3 + 3C_2H_4O} + 3H_2O.$$
$$Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O.$$
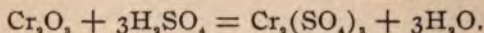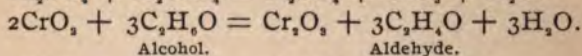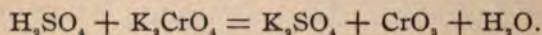
Experiment 157.—Fuse on platinum foil a little chrome alum with equal parts of sodium carbonate and potassium nitrate. Dissolve the fused mass in water and, after acidifying with acetic acid, add lead acetate to the solution. What is formed?

Experiment 158.—Treat a solution of potassium chromate with sulphuric acid. What change is there? Then add sodium hydroxid. Note any change.

Experiment 159.—To a solution of potassium chromate add hydrochloric acid and alcohol and warm. Note the odor of aldehyde formed and the change of color incident to the formation of a chromic compound.

423. Other Oxids of Chromium.—Other oxids of chromium are known but they are not very important. There is also a chromium oxychlorid which is sometimes called chlorochromic acid and from it a series of chlorochromates are formed. The formation of this body is made use of in separating the halogens in analysis.

424. Oxids of Molybdenum.—Molybdenum forms four oxids: the monoxid MoO, sesquioxid Mo_2O_3 dioxid MoO_2, and the trioxid MoO_3. The first three oxids are base-forming but only the chlorids and bromids are well known. The trioxid, MoO_3, is the chief oxid and is acid-forming, resembling CrO_3 and SO_3.

Molybdenum Trioxid, MoO_3

425. Preparation and Properties.—This oxid is found in nature, especially combined with lead. It is a white powder, melting and volatilizing without decomposition. It requires a large amount of water for its solution. This solution reddens litmus and acts as an acid. Molybdic acid, H_2MoO_4, is a yellow crystalline body and forms a variety of salts (molybdates). Ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, is more used than any of the series, large amounts of it being required for the determination of phosphoric acid in analytical laboratories.

426. Tungsten Oxids.—Tungsten forms two definite oxids and others which are perhaps compounds of these two. These two are the typical oxids of the group, tungsten dioxid, WO_2, and tungsten trioxid, WO_3. The

first of these, tungsten dioxid, forms compounds with the halogens and so acts as a base.

Tungsten Trioxid, WO_3

427. Preparation and Properties.—The trioxid occurs naturally. It is a yellow powder, soluble in alkalies, insoluble in water and acids. It forms tungstic acid, H_2WO_4, and metatungstic acid, $H_2W_4O_{13}.7H_2O$. These give tungstates and metatungstates. A large number of these salts are known. Thus there are ten or twelve sodium tungstates. Most of the tungstates are insoluble in water. Some are used as mordants and to render clothing non-inflammable. Calcium tungstate is also used on the screens for the X-rays. A number of tungsten '' bronzes'' are prepared by combining tungstates with the dioxid.

Uranium Oxids

428. Uranium Oxids.—Uranium forms two oxids, uranous oxid, UO_2, and uranic oxid, UO_3, and these combine to form a number of others as in the case of molybdenum. Among these is U_3O_8.

Uranium dioxid is base-forming, dissolving in strong acids to form uranous salts. These are green and not very stable, readily absorbing oxygen. Uranic oxid, UO_3, also enters into combination with strong acids giving salts in which a radical, UO_2, seems to play the part of an element. They may be considered as basic salts. This is called uranyl and the salts uranyl salts. Thus uranyl nitrate, $(UO_2)(NO_3)_2$. The hydroxid, $UO_2(OH)_2$, is an acid and unites with strong bases giving uranates. These correspond to the bichromates, for instance, $K_2U_2O_7$, potassium uranate.

THE SULPHIDS OF GROUP VI

None of the sulphids of Group VI possess any practical importance except molybdenum sulphid, MoS, which is the ore of molybdenum. In general they are analogous to the oxids and in the cases of molybdenum and tungsten, salts of the thioacids are known, as K_2MoS_4 and K_2WoS_4.

THE OXIDS OF GROUP VII

These oxids are acid-forming, or neutral. The types are M_2O and M_2O_7. Fluorin has, as yet, yielded no oxid nor oxyacid.

429. Chlorin Oxids.—Chlorin forms three oxids, Cl_2O, Cl_2O_3, and Cl_2O_4 or ClO_2. There are besides four oxyacids, two of which correspond to two unknown oxids. These oxids are all unstable and some of them quite explosive. None can be formed by direct means. The acids are more stable and some of their compounds are very useful.

Chlorin Monoxid, Cl_2O

430. Preparation and Properties.—This oxid is prepared by passing chlorin over mercuric oxid.

$$HgO + 2Cl_2 = HgCl_2 + Cl_2O.$$
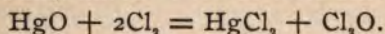
It is a reddish yellow gas with a penetrating odor like chlorin. It can be condensed to a liquid at a low temperature. It has a specific gravity of 3.0, and is soluble in water forming hypochlorous acid. On warming, it explodes. It has a great oxidizing power.

431. Hypochlorous Acid, HClO.—This acid cannot be prepared free from water. It can be obtained in solution by the action of an acid upon the solution of a hypo-

chlorite. It is a weak, unstable acid, with a peculiar odor, and exhibiting strong oxidizing and bleaching action. It is very easily decomposed. Although the acid is so unstable, its compounds, the hypochlorites, are very useful and are manufactured in enormous quantities. The alkaline hypochlorites are prepared by passing a stream of chlorin through a cold, dilute solution of the hydroxid.

$$2KOH + Cl_2 = KClO + KCl + H_2O.$$
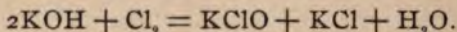
They are not separated in the pure form but are used in aqueous solution. These alkaline hypochlorites are now substituted by calcium hypochlorite which can be prepared much more cheaply. Calcium hypochlorite is obtained by passing chlorin over moist lime. The result seems to be a compound of hypochlorite and chlorid, $Ca(ClO)_2.CaCl_2$. This is always mixed with a considerable amount of unchanged calcium hydroxid and with some calcium chlorid. It is easily decomposed by acids, even the carbon dioxid of the air having this action. It, therefore, cannot be preserved in its original strength for any great length of time. It is called chlorid of lime which must be distinguished from calcium chlorid. More commonly, it is called bleaching-powder or " bleach." It is used very largely for bleaching purposes and as a disinfectant. For bleaching it must be used in conjunction with some acid so as to set the hypochlorous acid free for it is this hypochlorous acid which does the bleaching. The action is one of oxidation.

$$Ca(ClO)_2 + H_2SO_4 = CaSO_4 + 2HClO.$$
$$HClO = HCl + O.$$
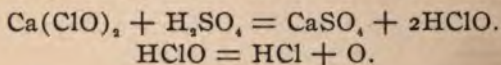
Many thousands of tons of bleaching-powder are made annually. It must not be kept in tightly stoppered vessels because of its decomposition and the liberation

of gases which collect and might burst the vessel with explosive violence.

Experiment 160.—To a little bleaching-powder in solution add a few drops of sulphuric acid. Note the odor and bleaching power.

Chlorin Trioxid, Cl_2O_3

432. Preparation and Properties.—This is prepared by the reduction of chloric acid. Dilute sulphuric acid is warmed with potassium chlorate in the presence of sugar or oxalic acid. Chloric acid is first formed and then gives some of its oxygen to the sugar. This is an operation which must be carried out with great care. The trioxid is a green unstable gas with a very pungent irritating odor, soluble in water and decomposed by heat, light, and oxidizable matter.

433. Chlorous Acid, $HClO_2$, is formed by the solution of chlorin trioxid in water. It cannot be separated from solution. This is a weak acid easily decomposed and forms chlorites which are unstable.

Chlorin Tetroxid, Cl_2O_4 or ClO_2

434. Preparation and Properties.—The formula for this body should probably be written ClO_2. It is formed by the action of strong sulphuric acid upon potassium chlorate. It is a heavy, dark yellow gas, and can be condensed to a red liquid. It is soluble in water, has a peculiar odor, is unstable, and is a powerful oxidizing agent. Thus, if it is prepared in the presence of phosphorus or of sugar and other forms of organic matter, these will be set on fire. The solution in water contains chlorous acid, $HClO_2$, and chloric acid, $HClO_3$. The oxid is decomposed by water and may be a compound of Cl_2O_3 and Cl_2O_5. It yields the oxyacids corresponding to these two oxids and none peculiar to itself.

435. Chloric Acid, $HClO_3$.—This acid would correspond to a pentoxid, Cl_2O_5, but no such oxid is known. It is formed by the addition of an acid to a chlorate. The chlorates are obtained by passing chlorin through a strong warm solution of an alkaline hydroxid. At the same time the chlorid is formed but there is no combination of this chlorid with the chlorate.

$$3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O.$$
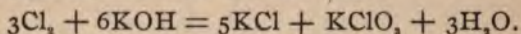
The chlorate crystallizes out from the solution first in large tabular crystals as it is the least soluble. Potassium chlorate is now made chiefly by the electrolysis of a solution of potassium chlorid.

It is to be noted that when chlorin acts on potassium hydroxid the hydroxyl group, OH, is liberated which at once decomposes, forming water and liberating oxygen. If the solution is cold, the potassium chlorid is by this oxygen oxidized to KClO but if hot, then it is oxidized to the more stable $KClO_3$.

All chlorates are soluble in water and many deliquesce. Potassium chlorate is the most important. It is a white crystalline body, quite stable until heated when it loses oxygen and becomes changed into the chlorid.

$$KClO_3 = KCl + O_3.$$
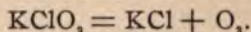
It is easily decomposed by means of strong acids. It is used medicinally, and also in the preparation of oxygen and explosives. Chloric acid, $HClO_3$, is known only in solution. It is very unstable, and both bleaches and oxidizes. This latter action may be so great as to set paper, etc., on fire.

Experiment 161.—To a very small quantity of potassium chlorate ($KClO_3$) add a drop of concentrated sulphuric acid. Warm the evolved gas gently. Use great care.

Experiment 162.—Treat a little potassium chlorate with concentrated hydrochloric acid. What is evolved?

Experiment 163.—Mix a little potassium chlorate and sugar and touch with a stirring rod which has been dipped in concentrated sulphuric acid.

Experiment 164.—In the bottom of a reagent glass put a piece of phosphorus, about as large as a pea, and a few crystals of potassium chlorate. Then fill the glass nearly full of water. Pour, cautiously, a little concentrated sulphuric acid through a funnel pipette extending to the bottom of the glass. What is the reaction?

436. Perchloric Acid, $HClO_4$.—This is prepared by adding an acid to a perchlorate.

$$BaClO_4 + H_2SO_4 = BaSO_4 + HClO_4.$$
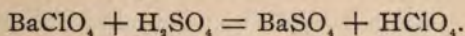
The perchlorates are prepared by heating the chlorates until one-third of the oxygen is lost.

$$2KClO_3 = KClO_4 + KCl + O_2.$$
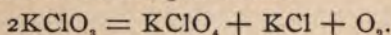
This is the only oxyacid of chlorin which can be freed from water and so prepared pure. It is a volatile, colorless liquid, fumes in the air, and sets fire to paper or wood because of the rapid oxidation. It is decomposed by heat. The perchlorates are also decomposed by heating. Perchloric acid would correspond to a heptoxid of chlorin, Cl_2O_7, which, however, has never been prepared.

The constitution of the four acids of chlorin can be expressed thus:

$$H—O—Cl \quad = \text{hypochlorous acid.}$$
$$HO—Cl=O = \text{chlorous acid.}$$

$$HO—Cl\begin{smallmatrix}\nearrow O \\ \searrow O\end{smallmatrix} = \text{chloric acid.}$$

$$HO—Cl\begin{smallmatrix}\nearrow O \\ =O \\ \searrow O\end{smallmatrix} = \text{perchloric acid.}$$
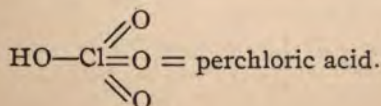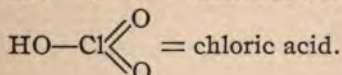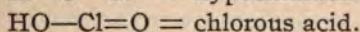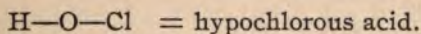
437. Bromin Oxids.—Bromin has so far yielded no oxid. There are three oxyacids which are known, hypobromous acid, HBrO, bromic acid, $HBrO_3$, and perbromic acid, $HBrO_4$.

438. Hypobromous Acid, HBrO.—This would correspond to a bromin monoxid, Br_2O. It is formed in a manner similar to hypochlorous acid and has similar properties, forming hypobromites. A bromid of lime can be prepared. Its bleaching power is less than that of the corresponding chlorin compound.

Sodium hypobromite, NaOBr, corresponding to the hypochlorite, is formed by adding bromin to a solution of caustic soda.

$$2NaOH + Br_2 = NaBr + NaOBr + H_2O.$$
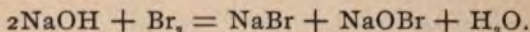
It is a bleaching agent, and is also used in the laboratory in the determination of urea, $CO(NH_2)_2$, which is decomposed by it into carbon dioxid, nitrogen, and water.

The hypochlorites and hypobromites react with ammonia, the latter in the cold, with evolution of nitrogen.

$$3NaOBr + 2NH_3 = 3NaBr + N_2 + 3H_2O.$$
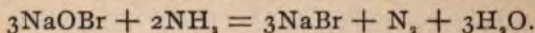
439. Bromic Acid, $HBrO_3$.—Bromates can be formed in the same manner as the chlorates and resemble them in their properties. They can be decomposed by an acid and bromic acid obtained, with properties like those of chloric acid.

440. Perbromic Acid, $HBrO_4$.—This is said to be formed by the action of bromin upon dilute perchloric acid. This shows that bromin can substitute chlorin in the oxycompounds.

441. Iodin Oxids.—Iodin forms one oxid, I_2O_5, and three oxyacids, though one of these, hypoiodous acid, is not known in a pure condition. Very unstable hypo-

iodites can be formed by methods similar to those used in the preparation of hypobromites.

Iodin Pentoxid, I_2O_5

442. Preparation and Properties.—This oxid is formed by heating iodic acid. It is a white powder, soluble in water and decomposed by heating. It has oxidizing properties.

443. Iodic Acid, HIO_3, is prepared by dissolving iodin in concentrated nitric acid. On heating this hydroxid, water is lost and I_2O_5 formed. On further heating, this oxid is decomposed into iodin and oxygen. The acid has the power of bleaching and is a strong oxidizing agent. A number of its compounds, iodates, are known. Sodium iodate, $NaIO_3$, is sometimes found in nature, occurring along with sodium nitrate.

Periodic Acid, HIO_4

This would correspond to iodin heptoxid, I_2O_7, which is unknown. The acid can be obtained by adding iodin to perchloric acid.

$$I + HClO_4 = HIO_4 + Cl.$$
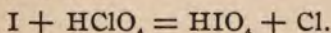
This shows that iodin can substitute chlorin in its oxy-compounds. It can also substitute bromin. Periodic acid, HIO_4, is a colorless, crystalline, deliquescent solid. It is decomposed at 140° and has a strong acid reaction. It is a powerful oxidizing agent. The periodates can be formed by heating the iodates. They are very numerous and complex.

444. Manganese Oxids.—Manganese forms a number of oxids of which the most important are MnO, Mn_2O_3, Mn_3O_4, MnO_2, and Mn_2O_7. Manganese shows an analogy to chromium in its oxids and their compounds. At the

same time it is noticeable that it is the only one of this group to form the heptoxid as well as the acid derived from it. The first two oxids are base-forming, the last is acid-forming, and there is one acid corresponding to an unknown oxid, MnO_3. The dioxid is neutral. Three of these oxids, Mn_2O_3, Mn_3O_4, and MnO_2, are found in nature.

Manganese Monoxid, Manganous Oxid, MnO

445. Preparation and Properties.—This is obtained by heating some of the higher oxids in hydrogen. It is a stable, greenish powder, forming manganous salts, which are the chief salts containing this element as base. They are colored pink and some absorb oxygen, especially when moist. Others as the sulphate, nitrate, and chlorid, are very stable crystalline compounds.

Manganese Sesquioxid, Manganic Oxid, Mn_2O_3

446. Preparation and Properties.—This occurs naturally. It may be obtained by heating the other oxids in oxygen. With acids it forms the manganic salts which are purple red in color. The most important of these is the sulphate.

Manganese Red Oxid, Mn_3O_4

447. Preparation and Properties.—This also occurs in nature. It is obtained whenever any of the other oxids is heated in air. It is looked upon as a compound of the first two oxids. It gives no salts with acids nor does it form an oxyacid.

Manganese Dioxid, MnO_2

448. Preparation and Properties.—This is known as the black oxid of manganese. Mineralogically it is called pyrolusite. It occurs quite widely distributed

and in fair abundance, and is the chief ore of manganese. It is formed when oxidizing agents, as the hypochlorites, are added to the manganous salts in solution. It is a black substance and is used for preparing oxygen and chlorin, and in coloring glass. Its mineralogical name (pyrolusite, washing by fire) was given by the ancients because from very early times small quantities of it have been used to neutralize traces of color in glass. As it is the chief ore of manganese the compounds of manganese are mainly prepared from it. It combines with several strongly positive oxids to form compounds called manganites which may be considered salts of a manganous acid, $H_2Mn_5O_{11}$. Little is known of these compounds.

449. Manganic Acid, H_2MnO_4.—This would correspond to a manganese trioxid, MnO_3, but no such body is known to exist; nor is the acid itself known in the free state. Its compounds, the manganates, are prepared by fusing manganese dioxid or other manganese compounds with alkaline hydroxids and some oxidizing agent as potassium chlorate. The manganates are green bodies, and quite unstable (more stable in the presence of a large excess of alkali). The alkaline manganates are soluble in water. The green solutions are decomposed by carbon dioxid or by dilution and exposure to the air. The manganates, M_2MnO_4, correspond in formula to the sulphates, M_2SO_4. They are strong oxidizing agents and are used as disinfectants.

Manganese Heptoxid, Mn_2O_7

450. Preparation and Properties.—The heptoxid is obtained by adding cool concentrated sulphuric acid to potassium permanganate. It is a dark oily liquid and

is very unstable, decomposing violently on warming or on coming in contact with organic matter.

451. Permanganic Acid, $HMnO_4$.—This acid may be prepared by using dilute sulphuric acid in the place of the concentrated acid used in the last reaction. It is a red liquid decomposed by heat and organic matter. It is a powerful oxidizing agent. The chief salt is potassium permanganate which is prepared from potassium manganate by passing carbon dioxid through a solution of it. The salt forms very dark purplish red crystals, giving a red powder and a purple solution. It is a powerful oxidizing agent, and is largely used for this purpose and as a disinfectant. The permanganates correspond in formula to the perchlorates, having the

constitution $KO—Mn{\displaystyle \mathop{=}^{/\!\!/O}_{\diagdown O}}O$.
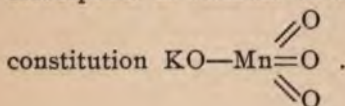
THE SULPHIDS OF GROUP VII

The sulphids of the halogens have been mentioned under the halids. Two sulphids of manganese occur in nature, manganese sulphid, MnS, and manganese disulphid, MnS_2. Manganese sulphid is formed when manganous salts are precipitated by an alkaline sulphid.

$$MnCl_2 + (NH_4)_2S = MnS + 2NH_4Cl.$$
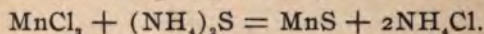
Another sulphid of manganese is also known, Mn_3S_4.

Experiment 165.—Fuse manganese dioxid on platinum foil with potassium nitrate and sodium carbonate. Examine the potassium manganate (K_2MnO_4) formed.

Experiment 166.—Reduce a solution of potassium permanganate ($KMnO_4$) with hydrogen sulphid and with alcohol.

THE OXIDS OF GROUP VIII

452. General Characteristics.—The elements with lower atomic weight have, like manganese, a strong tendency to form oxids analogous to those of Group II, as FeO, CoO, and NiO. Iron and cobalt, like chromium, form oxids analogous to those of Group III, as Fe_2O_3, and Co_2O_3; and these two elements also form oxids of a type analogous to Mn_3O_4; *viz.*, Fe_3O_4 and Co_3O_4.

Iron, ruthenium, and osmium form salts analogous to those of Group VI, as K_2FeO_4, K_2RuO_4, and K_2OsO_4, derived from acid-forming oxids, FeO_3, RuO_3, and OsO_3. The free oxids FeO_3 and RuO_3 are not known. The other elements, rhodium, iridium, palladium, and platinum each form several oxids but, like those of cobalt and nickel, they are all base-forming. Ruthenium and osmium form, in addition, volatile oxids, RuO_4 and OsO_4, which are not known either as acids or combined in the form of salts. These are the highest oxids known.

453. Iron Oxids.—Iron has three oxids, ferrous oxid, FeO, ferric oxid, Fe_2O_3, and ferrous-ferric oxid, Fe_3O_4.

Ferrous Oxid, FeO

454. Preparation and Properties.—This oxid is prepared by reducing ferric oxid with hydrogen. It is a black powder oxidizing readily and is unstable. The hydroxid, $Fe(OH)_2$, is formed by precipitation with an alkaline hydroxid taking care to exclude all oxygen. It is a white powder rapidly oxidizing to green and finally to red-brown ferric hydroxid. It is basic and forms a series of salts called ferrous salts. The most important of these is ferrous sulphate, $FeSO_4$, or copperas.

Ferric Oxid, Fe_2O_3

455. Preparation and Properties.—This oxid occurs as the most important ore of iron and is known as hematite. It may be formed by heating the hydroxid or any salt of iron in which the acid is volatile. It is a heavy brownish red powder, insoluble in water and difficultly soluble in acids after it has been ignited. It yields much of the iron of commerce and in some of its forms is used as a paint and for polishing steel, glass, etc.

456. Ferric Hydroxid, $Fe(OH)_3$, is prepared by precipitation, best with ammonium hydroxid. It is reddish brown in color and is the coloring-matter of many soils. In mass it is known as red ochre. It is soluble in acids, giving ferric salts. This oxid also combines directly with several oxids as those of lime, magnesia, zinc, etc.

Ferrous-ferric Oxid, Magnetic Oxid, Fe_3O_4

457. Preparation and Properties.—This oxid occurs in nature as magnetite and is called magnetic iron ore or the magnetic oxid. It is prepared by the union of iron and oxygen at high temperatures, as in the case of iron burning in oxygen or at the blacksmith's forge. It is magnetic and is a neutral oxid. It is probably a compound of ferrous and ferric oxids.

458. Ferric Acid, H_2FeO_4.—This acid would correspond to the oxid, FeO_3. No such oxid is known nor is the acid, H_2FeO_4, known in the free state. Several of its compounds are known, however. Potassium ferrate can be formed by fusing iron with potassium nitrate and by treating $Fe(OH)_3$, suspended in the solution of an alkaline hydroxid, with bromin. It has a purple color and is very unstable.

459. Cobalt Oxids.—Cobalt forms three oxids, cobaltous oxid, CoO, cobaltic oxid, Co_2O_3, and cobalto-cobaltic oxid, Co_3O_4.

Cobaltous Oxid, CoO

460. Preparation and Properties.—This oxid is prepared by reducing the higher oxid by means of hydrogen. It is a brown powder not altering in the air. It is insoluble in water, soluble in acids, and forms cobaltous compounds. The hydroxid, $Co(OH)_2$, is obtained by precipitation with an alkaline hydroxid in the absence of oxygen.

The cobaltous salts are the principal salts of cobalt. The silicate is largely used in blue glass and for blue paint. The chief remaining salts are the nitrate, sulphate, and chlorid. They are red and deliquescent as a rule. When deprived of water they are blue.

Cobaltic Oxid, Co_2O_3

461. Preparation and Properties.—This oxid is prepared by gently heating the nitrate. It is a dark brown powder. A hydroxid, $Co(OH)_3$, can be obtained by precipitation from a cobalt salt in the presence of an oxidizing agent. This compound is slightly basic, giving a few salts.

Cobaltous-cobaltic Oxid, Co_3O_4

462. Preparation and Properties.—This oxid is obtained as a black powder when either of the other oxids is heated in the air. It may be regarded as a compound of the cobaltous and cobaltic oxids. It is neutral. There is some evidence of the existence of compounds of a cobaltic acid which is analogous to ferric acid. A potassium cobaltate seems to be formed by fusing any of the oxids with caustic potash.

463. Nickel Oxids.—Nickel forms two oxids, nickelous oxid, NiO, and nickelic oxid, Ni_2O_3.

Nickel Monoxid, NiO

464. Preparation and Properties.—This oxid occurs in nature. It is prepared as a green powder by strongly heating the hydroxid or nitrate. The hydroxid, $Ni(OH)_2$, is precipitated by potassium or sodium hydroxid from a solution of a nickel salt. It is soluble in acids, giving nickelous, or simply nickel salts, as this is the only class. These are green and quite stable. The most important are the sulphate and cyanid.

Nickel Sesquioxid, Ni_2O_3

465. Preparation and Properties.—This oxid is obtained as a black powder by gently heating the nitrate in the air. It dissolves in sulphuric or nitric acid evolving oxygen, and in hydrochloric acid evolving chlorin. This behavior is characteristic of certain oxids which have been called the peroxids. The hydroxid, $Ni(OH)_3$, can be formed as in the case of cobalt. No salts are formed from this oxid.

466. Ruthenium Oxids.—Ruthenium forms six oxids, RuO, Ru_2O_3, RuO_2, RuO_3, Ru_2O_7, and RuO_4. Two of these, RuO_3 and Ru_2O_7, are known only in combination. They act as acids when combined with water and give respectively ruthenates and perruthenates. The tetroxid, RuO_4, is volatile at 100° and is explosive. Ruthenium salts are formed from the sesquioxid, but only a few are known.

467. Rhodium Oxids.—Rhodium forms three oxids, RhO, Rh_2O_3, and RhO_2. The sesquioxid alone forms salts; the dioxid forms a hydroxid which seems to be acid in character.

468. Palladium Oxids.—Palladium gives three oxids, Pd_4O, PdO, and PdO_2. The second, palladium monoxid, PdO, is the only one forming compounds. It forms a hydroxid, $Pd(OH)_2$, which acts as a base, giving palladious salts.

469. Osmium Oxids.—Osmium has five oxids, OsO, Os_2O_3, OsO_2, OsO_3, and OsO_4. The trioxid, OsO_3, is known only in its compounds, the osmates. It is acid-forming. The monoxid and sesquioxid act as bases and give classes of salts, osmous and osmic salts. The dioxid, OsO_2, is neutral. The tetroxid, OsO_4, is sometimes called osmic acid. It is volatile at 100°. The vapor has an irritating odor and is very poisonous.

470. Iridium Oxids.—Iridium forms two oxids and the hydroxid of a third, Ir_2O_3, IrO_2, and $Ir(OH)_4$. There seem to be three classes of salts corresponding to these, two of which are well known. In all of these, iridium acts as a base.

471. Platinum Oxids.—Platinum forms two oxids, platinous oxid, PtO, and platinic oxid, PtO_2, both of which are base-forming.

Platinum Monoxid, Platinous Oxid, PtO

472. Preparation and Properties.—This is obtained as a gray powder by carefully heating platinous hydroxid. On further heating the metal is obtained. The hydroxid is prepared by precipitating the chlorid with hot potassium hydroxid. It is soluble in some acids, is decomposed by alkalies, and is a weak base.

Platinum Dioxid, Platinic Oxid, PtO_2

473. Preparation and Properties.—The dioxid is prepared as a black powder by gently heating the hydroxid

which is formed by precipitating platinic chlorid with potassium hydroxid. This oxid yields platinates with strong bases and platinic salts with acids. On heating this oxid the metal is obtained.

THE SULPHIDS OF GROUP VIII

The sulphids of this group correspond quite closely to the lower oxids. Sulphids higher than the disulphid are unknown.

Several sulphids of iron are known, the most important of which are ferrous sulphid, FeS, formed by heating together iron and sulphur, and iron pyrites, FeS_2, which occurs in nature and is sometimes called fool's gold. Ferrous sulphid is a heavy black solid and is used in the laboratory for generating hydrogen sulphid.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$
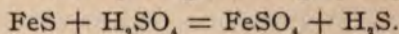
Iron pyrites is yellow-colored and is chiefly useful on account of the sulphur which it contains. Large quantities of it are burned for the production of sulphur dioxid in the manufacture of sulphuric acid.

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$
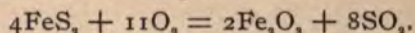
474. Selenids.—With regard to these compounds it may be stated that a few of them occur in nature, generally accompanying the sulphids. Others have been prepared by methods analogous to those used for the sulphids, which they resemble.

475. Tellurids.—These are rarer than the selenids and show a general analogy to them and the sulphids.

LAWS OF CHEMICAL COMBINATION

Since many chemical compounds have been studied and experimentally examined and tested in the preceding

pages, it is well to sum up here what knowledge has been gained as to the laws governing their formation. Three such laws will appear on a closer examination of the facts learned. All of these have to do with the proportions in which the elements combine.

476. Law of Constant Proportions.—In forming a definite compound, the elements always unite in constant fixed proportions. Thus water always contains 1 part by weight of hydrogen to 8 parts by weight of oxygen; hydrochloric acid has 1 part by weight of hydrogen to 35.4 parts of chlorin; sodium chlorid has 23 parts of sodium to 35.4 parts of chlorin, etc.

477. Law of Interproportionality.—If a compound is formed by each of two elements A and B with the same proportion of a third element C, then, if they combine with one another, it will be in the proportions in which they combined with C, or in simple multiples of them. Thus, taking two of the examples given under the first law, 8 parts of oxygen combine with 1 of hydrogen and again 35.4 parts of chlorin combine with 1 part of hydrogen; hence 8 parts of oxygen combine with 35.4 parts of chlorin.

478. Law of Multiple Proportions.—In the early part of this century Dalton, an English mathematician and physicist, discovered the law of multiple proportions, which may be expressed as follows:

If two elements form several compounds with each other, the proportions of one that combine with a fixed proportion of the other bear a simple relation to one another.

Thus 56 parts of iron combine with 16 parts of oxygen or with 24 parts (the proportion here is 2 : 3). Again

32 parts of sulphur combine with 32 parts of oxygen or with 48 parts (proportion 2 : 3); and 12 parts of carbon combine with 16 parts of oxygen or with 32 parts (proportion 1 : 2). A still more striking example is seen in the case of nitrogen. Here 28 parts of nitrogen combine, in five different compounds, with 16, 32, 48, 64, and 80 parts of oxygen respectively, and the proportions are 1 : 2 : 3 : 4 : 5. These facts are explained by the atomic theory since these compounds are built up of whole indivisible atoms. If we have two atoms of nitrogen, or 28 parts, combining with one atom of oxygen, or 16 parts, then the next compound must have twice as many parts of oxygen (or two atoms), or three times as many, or some whole number of times as many, and hence the relation must be a simple one. The formulas for these compounds would express this relation; thus: N_2O, N_2O_2, N_2O_3, N_2O_4, and N_2O_5.

Thus the only satisfactory explanation offered of these laws is embraced in the atomic theory. In all chemical combination we are dealing with atoms. It is atom or atoms uniting with atom or atoms and hence the recurrence noted of the weight of these atoms in the so-called proportions. It was the discovery of the Law of Multiples which immediately led up to the announcement by Dalton of the atomic theory.

PART VI

OTHER BINARY COMPOUNDS

BINARY COMPOUNDS OF GROUP V

479. Nitrids.—Nitrogen forms a series of compounds called nitrids but only a few of these are known. They are usually not well characterized and have been but little studied. They are formed by heating the element to a high temperature with nitrogen (or air) and the reaction seems to be assisted by the presence of some substance which will prevent the oxidation of the metal. Thus magnesium heated along with calcium carbid in an electric furnace yields the nitrid. One of the first known of these was boron nitrid. Lithium unites with nitrogen at ordinary temperatures forming the nitrid, Li_3N. These nitrids are generally decomposed by the addition of water, forming ammonia.

480. Sodium and Potassium Amids.—These bodies scarcely belong under this heading but may be mentioned here. When sodium or potassium is heated with ammonia, sodamid, $NaNH_2$, or potassamid, KNH_2, is formed which decompose with water with the evolution of ammonia (NH_3). By the action of nitrous oxid on sodamid, sodium hydrazoate is formed, thus:

$$NaNH_2 + N_2O = H_2O + NaN_3.$$
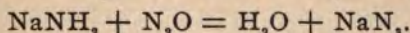
The hydrazoates are salts of hydrazoic acid (HN_3), and have already been described under the nitrogen hydrids.

481. Phosphids.— These are more numerous and better

known than the nitrids. Some, as those of copper and silver, can be formed by the simple addition of phosphorus to a solution of a copper or a silver salt; others are formed by the heating of phosphorus with the elements. Some, as calcium phosphid, are decomposed by water forming phosphin (PH_3); others are decomposed by dilute acids. The formation of copper phosphid is sometimes resorted to in cases of phosphorus poisoning or where phosphorus, in small pieces, has gotten under the finger nails or in crevices of a table or floor. As soon as a dilute solution of copper sulphate comes in contact with the phosphorus, the phosphid is formed, which is comparatively harmless as it is insoluble and oxidizes slowly.

Arsenids, antimonids, and similar compounds with the remaining elements of Group V, fall more properly under the head of alloys.

Experiment 167.—Add a small piece of phosphorus to a solution of copper sulphate.

* * *

BINARY COMPOUNDS OF GROUP IV

482. Carbids.—Carbids have become of late years a very important class of bodies. They are usually formed by the intense heating of carbon with the element or its oxid or carbonate. Thus it is recognized that many of the peculiar properties of pig iron are due to the carbid of iron which it contains and which is formed by the intense heat of the blast-furnace. There are several carbids of iron. To one the formula Fe_4C has been assigned.

For the formation of most of the carbids, however, the heat of the electric furnace is required. The first one was formed by Davy in 1808. This was potassium carbid. In 1862 Wöhler discovered calcium carbid,

CaC_2. This is the most important of the carbids and it is now manufactured on a large scale by heating coke and lime in the electric furnace. It is a dense black substance, with crystalline fracture, and is easily decomposed by the addition of water forming acetylene.

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$
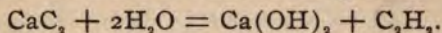
As acetylene gives a very brilliant light when burned and is otherwise a very interesting and useful body, calcium carbid is an important substance commercially.

483. Silicon Carbid, or carborundum, is also manufactured in large quantities. It is produced by heating together in the electric furnace, coal, sand, and sodium chlorid. A lustrous, crystalline substance is obtained which is the next to the diamond in hardness and finds large use as a polishing material and in the manufacture of steel.

A number of other carbids have been produced by Moissan and others in the electric furnace. Most of these are decomposed by the addition of water forming acetylene, C_2H_2, or methane, CH_4. Others are decomposed by dilute acids forming various hydrocarbons.

Compounds of Carbon and Nitrogen, or Cyanids

484. Cyanogen, $(CN)_2$, $N{\equiv}C{-}C{\equiv}N$.—Carbon and hydrogen unite under the influence of alkalies at high temperatures with the formation of alkaline cyanids, as potassium cyanid, KCN. Cyanogen is formed by heating mercuric cyanid.

$$Hg(CN)_2 = Hg + (CN)_2.$$
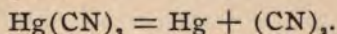
It is a colorless gas which is easily condensed to a liquid. Cyanogen is very poisonous, insoluble in water, and burns with a purple flame. Its constitution is probably $N{\equiv}C{-}C{\equiv}N$.

485. Hydrogen Cyanid, HCN.—This is called hydrocyanic acid, or prussic acid. It is formed by the action of acids on the cyanids.

$$KCN + HCl = KCl + HCN$$
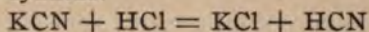
It is a colorless liquid, boiling at 26°, giving a very poisonous gas with a bitter almond odor. It is very soluble in water. Hydrocyanic acid is one of the weakest acids, scarcely reddening blue litmus, while some of its salts are partially decomposed by the carbon dioxid and water of the atmosphere. It is found in nature in a state of combination in amygdalin, which is a constituent of some leaves and of the kernels of certain stone fruit and of bitter almonds.

486. Cyanids.—There are a large number of compounds of hydrogen cyanid called cyanids, some of which are quite stable and useful. These bodies are generally studied at length under organic chemistry. Some will be briefly mentioned here.

487. Potassium Cyanid, KCN.—This is obtained by heating potassium ferrocyanid to decomposition and dissolving out the cyanid formed. It is a white solid, very soluble in water and easily decomposed by acids with the evolution of hydrogen cyanid. It can be fused without decomposition. It has a great affinity for oxygen at a high temperature and hence is a strong reducing agent. It unites with oxygen to form potassium cyanate, KCNO.

The cyanids bear a strong resemblance to the halids and have a similar but stronger tendency to form double salts. The cyanids of the alkalies and alkaline earths are soluble in water, the others insoluble.

488. Double Cyanids.—Two classes of double cyanids exist, the one separated into its components by acids, the other not so decomposed.

An example of the first type is given by silver cyanid, which is precipitated from solutions of silver salts by potassium cyanid. An excess of potassium cyanid dissolves the silver cyanid, forming double cyanid, AgCN.KCN. On the addition of an acid, this is decomposed and silver cyanid, AgCN, reprecipitated. This double cyanid is used in silver-plating. Because of this formation of soluble double cyanids, potassium cyanid is largely used in extracting gold (and silver) from their ores. The second type is illustrated by the double iron cyanids.

489. Potassium Ferrocyanid, $K_4Fe(CN)_6$.—This is formed by heating together nitrogenous organic matter, blood, horn, etc., with potassium hydroxid (or carbonate) in the presence of iron. This may be looked upon as $4KCN.Fe(CN)_2$. This is not decomposed by acids with the precipitation of the ferrous cyanid, but hydroferrocyanic acid, $H_4Fe(CN)_6$, is formed. From it, potassium cyanid and all other cyanogen derivatives are directly or indirectly prepared. It is used for the production of Prussian blue.

490. Potassium Ferricyanid, $K_3Fe(CN)_6$, is formed by the oxidation of the ferrocyanid by chlorin and water. It may be written $3KCN.Fe(CN)_3$.

Experiment 168.—Test a very dilute solution (1 drop to a testtube of water) of ferrous sulphate and of ferric chlorid, with potassium ferrocyanid, $K_4Fe(CN)_6$, and with potassium ferricyanid, $K_3Fe(CN)_6$, and with potassium thiocyanate, KCNS.

491. Silicids have been made by methods similar to those used for the production of the carbids. They have been little studied as yet. Magnesium silicid, Mg_2Si, is formed by the action of magnesium on silica.

$$SiO_2 + 4Mg = 2MgO + Mg_2Si.$$
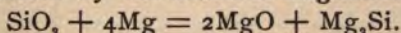
When treated with water or acids, silicon hydrid, SiH_4, is evolved.

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4.$$
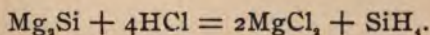
INTERCOMBINATION OF GROUPS I, II, and III

492. Alloys.—Generally where two or more positive elements are melted together the resulting product seems to be rather a mixture than a compound. Such characteristics of compounds as the possession of definite and constant composition, etc., are lacking. Therefore these are sometimes called indefinite compounds. The common name for them is *alloys*, or, if mercury be one of them, *amalgams*. There are a great number of these alloys and they are very useful, often more useful than either of the original elements composing them. Some elements will not alloy with one another. Thus iron forms few alloys while copper forms a great number. Iron will not alloy with copper. As a rule in alloys the melting-point is lower than that of either of the components and the specific gravity is greater than the mean. Some of the more important alloys are brass (copper and zinc), bronze (copper and tin), solder (lead and tin), etc.

NOTE

Since the first portion of this book was printed Dewar has succeeded in liquefying both hydrogen and helium. All known gases have, therefore, been condensed into the liquid form. The boiling-point of liquid hydrogen has been found to be $-238°$ or $35°$ absolute. The approximate density of liquid hydrogen at its boiling-point is slightly less than 0.07. Also the discovery of three new elements in the atmosphere has been announced by Ramsay. He has given these elements the names krypton, neon, and metargon. All resemble argon in properties.

APPENDIX

THE METRIC SYSTEM OF WEIGHTS AND MEASURES

In chemistry, as in all other sciences, the metric or decimal system of weights and measures is used. The advantages of this system are its decimal relations and the connection of its units of weight and volume with one standard unit.

The standard unit of the system is the meter (m.) = 39.37 inches, which is one ten-millionth of the quadrant of the earth's meridian passing through Paris. The meter is divided into centimeters (cm.) = 0.01 m. and millimeters (mm.) = 0.001 m. Rarely the denomination of decimeter = 0.1 m. is used.

Volume is measured by the cubic centimeter (cc.) and by the liter (l.) = 1000 cc. The liter is about 2.2 pints. The unit of weight is the gram (gm.) = 15.45 grains, which is the weight of one cubic centimeter of distilled water at 4° C. measured at the sea-level at Paris. The other denominations of weight are centigram (cg.) = 0.01 gm. and milligram (mg.) = 0.001 gm., and the kilogram (k.) = 1000 gms. The kilogram is commonly called kilo and is approximately 2.2 pounds.

Exercise a.—Estimate in the metric system the length of several objects in the laboratory ; then measure them accurately and compare the results.

Exercise b.—Do the same with the length and breadth of a page of a note-book, and with several lines of different lengths drawn in it. Record the results.

Exercise c.—Take a quantity of water in a small beaker and estimate the number of cubic centimeters it contains, and then

measure the same in a graduate. Do the same with test-tubes and other beakers of different sizes.

Exercise d.—Place on a silver quarter as much salt as it will hold and estimate its weight in grams. Verify by weighing on the balances.

Exercise e.—Place a paper on the scale pan and pour on by estimation 50 gms. of any salt. Then balance by weights. Do the same with 100 gms. and 150 gms. and repeat till an approximate estimation can be made.

THERMOMETRY.

In scientific work temperature is measured in centigrade degrees. In this scale the melting-point of ice is taken as $0°$ and the boiling-point of water as $100°$. These points in the Fahrenheit scale are respectively $32°$ and $212°$, and the interval between them is $180°$. Hence 100 centigrade degrees are equal to 180 Fahrenheit degrees, and $1° \text{ C} = \frac{9}{5} ° \text{ F.}$ and $1° \text{ F} = \frac{5}{9} ° \text{ C.}$ To change from °F to °C we have $°C = \frac{5}{9} (°F - 32°)$; and to change from °C to °F we have $°F = \frac{9}{5} °C + 32°$.

Exercise f.—Take the temperature of a beaker of water with a Fahrenheit thermometer. Calculate from this what it should be in centigrade degrees and verify the result with a centigrade thermometer.

Exercise g.—Warm some water in a beaker and estimate its temperature by the finger. Verify with a thermometer (centigrade).

Exercise h.—Estimate the temperature of the room (centigrade) and verify.

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